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EVALUATION OF ELECTROCHEMICAL ORGANIC CONTENT
ANALYZER FOR ARMY WATER SUPPLY TECHNOLOGY

R. J. Davenport, et al

Life Systems, Incorporated
Cleveland, Ohio

April 1980

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FINAL REPORT
(ANALYZER EVALUATION)

by

R. J. Davenport and J. B. Lantz

April, 1980

Supported by

US Army Medical Research and Development Command
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Life Systems, Inc.

Cleveland, OH 44122

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Army-related applications for the EOC Analyzer have been surveyed. Applications in which the EOC Analyzer may be used effectively are (1) monitoring activated carbon and synthetic adsorbent columns used for removal of organic contaminants from munitions wastes, metal finishing wastes and other wastewaters treated in physical-chemical treatment systems, (2) monitoring adsorption, coagulation or sedimentation processes for removal of the precursors of trihalomethane formation in drinking water, (3) monitoring and controlling biological wastewater

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treatment for process optimization and (4) monitoring oil and grease removal systems.

The EOC Analyzer was tested for possible use as a monitor of polyelectrolyte addition in the Reverse Osmosis Water Purification Unit developed by the U. S. Army Mobility Equipment Research and Development Command. The Analyzer was too sensitive to the organics in the water to be successfully used in that application, but an on-line turbidimeter, tested in parallel, provided the necessary response characteristics.

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LIFE SYSTEMS, INC.
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U.S. ARMY MEDICAL BIOENGINEERING
RESEARCH AND DEVELOPMENT LABORATORY
Ft. Detrick, Frederick, MD 21701

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U.S. Army Medical Bioengineering
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Ft. Detrick, Frederick, MD 21701

EXECUTIVE SUMMARY

The Electrochemical Organic Content Analyzer is a unique monitor of organic contaminants in water. It is capable of automated, on-line operation, and responds with high sensitivity to many relatively high molecular weight organics and aromatic compounds. The value of an organic solute monitor with these characteristics in process monitoring and control applications motivated a survey of Army-related applications for the Analyzer during this program (DAMD-17-79-C-9058). The Analyzer also was tested as a possible monitor of polyelectrolyte addition to drinking water treated by filtration in the Reverse Osmosis Water Purification Unit developed by the U.S. Army Mobility Equipment Research and Development Command. In this evaluation the performance of the Analyzer and an on-line turbidimeter (a more traditional instrumental method of monitoring polyelectrolyte addition) were compared.

The evaluation demonstrated that the Electrochemical Organic Content Analyzer is apparently so responsive to organic compounds in natural water samples that its response to the polyelectrolyte is insignificant in comparison. The turbidimeter, however, demonstrated the analytical characteristics required for a polyelectrolyte controller.

The response of the Electrochemical Organic Content Analyzer to organics in natural water samples supports earlier conclusions that the Analyzer would be responsive to large molecular weight organics and aromatic compounds, such as humic and fulvic acids, contained in natural waters and wastewaters.

The application survey identified four processes for which the Analyzer seems to be especially suited. The Analyzer may be useful in monitoring activated carbon and synthetic adsorbent column effluents applied to the treatment of munitions wastes, metal finishing wastes, or used as part of physical-chemical wastewater treatment systems. The Analyzer would detect the breakthrough of organics from the adsorbent column to indicate the need for regeneration, or to automatically trigger the adsorbent regeneration process. Use of the Analyzer would prevent discharging contaminated effluents, while avoiding the costs of unnecessary adsorbent regeneration.

The adsorption, coagulation and sedimentation processes used for removal of organics from raw water to prevent trihalomethane formation during disinfection may also be monitored by the Analyzer. Biological treatment processes may be monitored and controlled using the Analyzer, and it may be applicable to monitoring oil and grease removal systems.

Conclusions and recommendations are presented.

FOREWORD

The information collection and the experimental work described herein was performed by Life Systems, Inc. under U.S. Army Contract DAMD17-79-C-9058 during the period May 1, 1979 to April 30, 1980. The program was directed by Dr. R. J. Davenport. The technical effort was completed by Dr. R. J. Davenport, Dr. J. B. Lantz, Ms. J. R. Torrey, Mr. L. E. Wolfe and Dr. R. A. Wynveen.

Mr. William J. Cooper and Dr. Steve Hoke were the Contract Officer's Technical Representatives for the U.S. Army Medical Bioengineering Research and Development Laboratory, Ft. Detrick, Frederick, MD 21701.

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LIST OF ACRONYMS

BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
EOC	Electrochemical Organic Content
TOC	Total Organic Carbon

INTRODUCTION

The U.S. Army Medical Bioengineering Research and Development Laboratory (MBRDL) has played a significant role in the development of technology related to environmental protection. Among this technology is the Electrochemical Organic Content (EOC) Analyzer, which was developed with the goal of creating a simple, low-cost monitor of organic contaminants in treated wastewater effluents. The application for which this development was undertaken was the ozonation of hospital wastewaters.[1] The development of the Breadboard EOC Analyzer, under Contract No. DAMD17-75-C-5070, successfully demonstrated the EOC concept.[2-5]

Although the Breadboard EOC Analyzer was designed specifically for monitoring effluents that were treated by ultrafiltration (UF), reverse osmosis (RO) and ozonation (i.e., the Analyzer was not expected to encounter samples having large concentrations of organics, particulates or salts), it was also evaluated for other applications in which more contaminated samples were used. For example, the Analyzer was evaluated as a monitor of fire fighting foam in wastewaters treated by RO, carbon adsorption and air flotation.[5] Tests were also performed to evaluate the Analyzer as monitor of organic loading in shower and laundry wastewaters treated by RO.[6] The results of these tests indicate that the development of more advanced versions of the Analyzer is justified.

This report summarizes the results of a survey of new applications for the EOC Analyzer and an evaluation of the EOC concept for monitoring and controlling polyelectrolyte addition within the U.S. Army's Reverse Osmosis Purification Unit (ROWPU). During this evaluation, a performance comparison was made between the EOC Analyzer and on-line turbidimeter (a more traditional instrumental approach to polyelectrolyte monitoring).

Breadboard EOC Analyzer

The Breadboard EOC Analyzer is shown in Figure 1, and Figure 2 is a functional block schematic of the Analyzer. The sample enters the Analyzer, is mixed with electrolyte to maintain a fixed conductivity and pH, and the mixture flows through a temperature controller which maintains the solution at 25 C. The solution enters the solenoid valve and flows either through the electrochemical cell or the cell bypass loop, and on through a pump and backpressure regulator, which helps maintain a constant pumping rate.

Solution in the electrochemical cell is analyzed after electrochemical reduction of oxygen (O_2) dissolved in the electrolyte/sample mixture:

$$O_2 + 2H_2O + 4e^- = 4 \ OH^- \tag{1}$$

The organic concentration is determined by adsorbing a portion of the organic solutes in the solution onto the surface of the indicating electrode in the electrochemical cell. The decrease in the interfacial capacitance at the electrode/solution interface is measured and related to the organic concentration. A more complete summary of the Analyzer's operation has been reported.[5]

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(1) References cited at end of report.
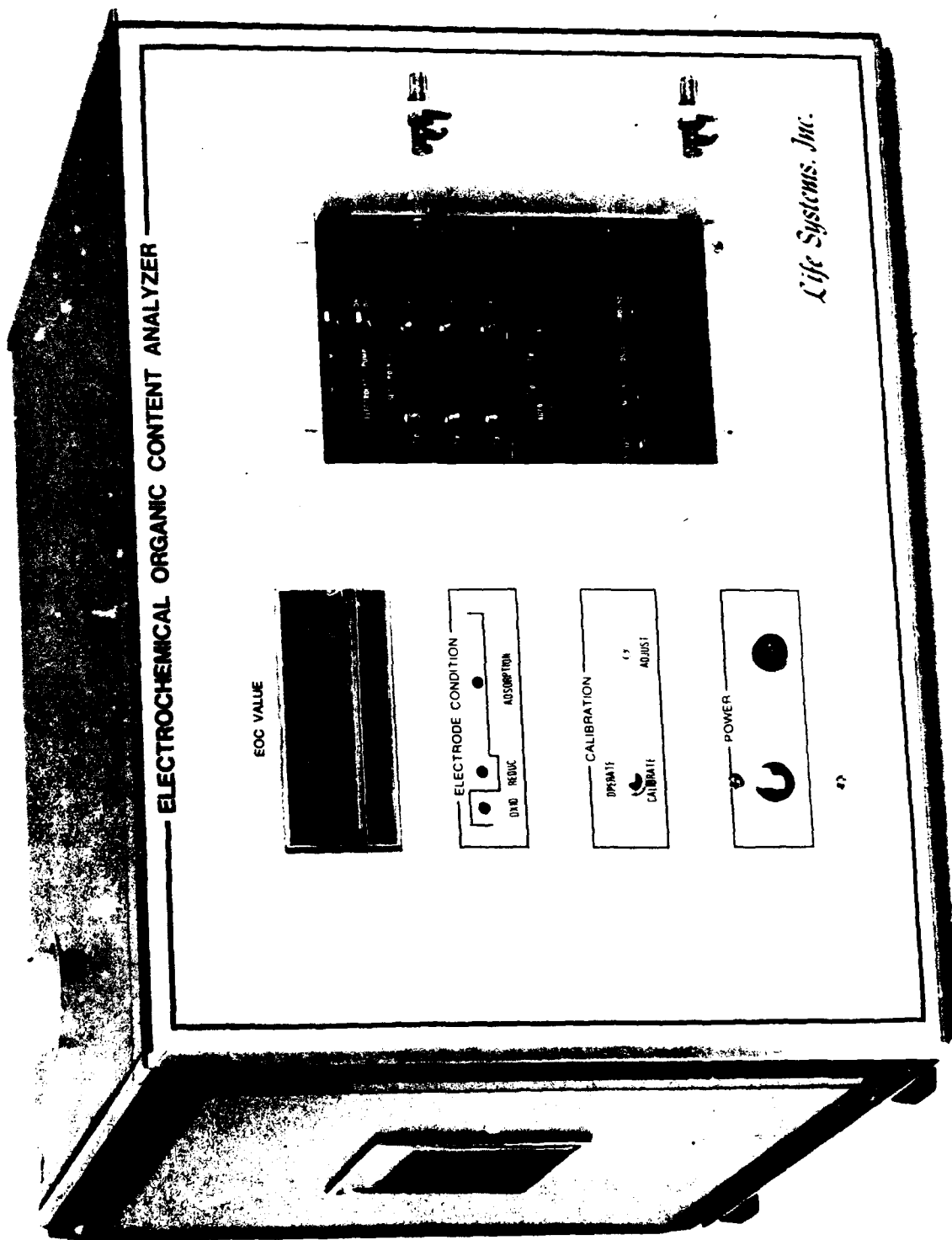
FIGURE 1 BREADBOARD EOC ANALYZER
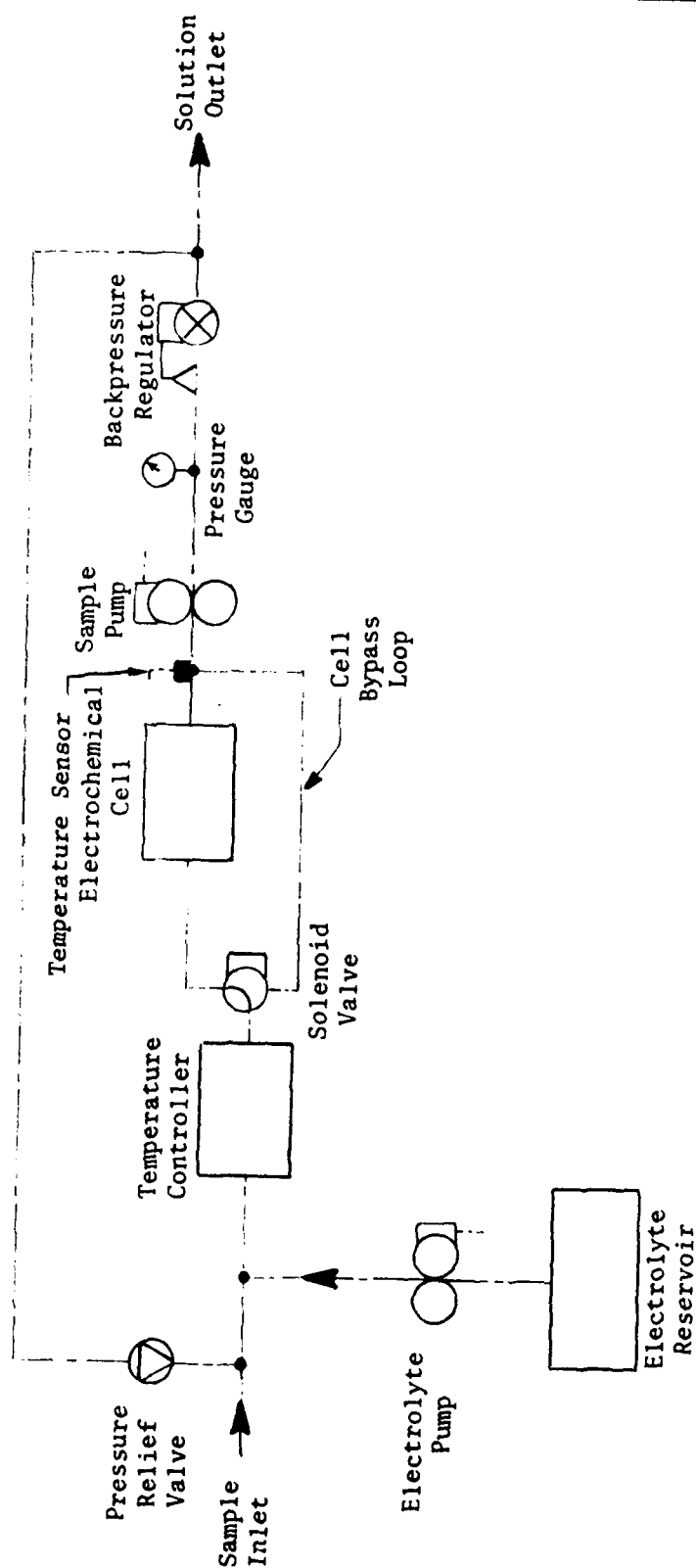
FIGURE 2 MECHANICAL SCHEMATIC OF BREADBOARD EOC ANALYZER

More advanced versions of the EOC Analyzer will be simplified by utilizing electronic temperature compensation in place of the temperature controller, simplifying the pumping system, incorporating autocalibration and other labor saving features.

Tests have shown that the EOC Analyzer responds to the general organic content of water similar to the way that conductivity monitors respond to the general concentration of ions. Some ions produce a large conductivity change, while other ions at the same concentration produce a smaller change. The total conductivity for a sample containing a mixture of ions is therefore only a general indicator of the water quality.

In many applications, conductivity monitors are used because a general indication of the ionic content of the water is desired. In other cases, the concentration of specific ions is desirable, and conductivity monitors are used because the response of the monitor can be correlated to the concentration of those specific ions. Conductivity monitors are simple, inexpensive and can be automated. These are significant advantages over other more specific analytical methods for many water quality monitoring and process control applications.

The EOC Analyzer is considered to be the organic analog of conductivity monitors.[6] Its response to specific organics is dependent upon the degree to which they adsorb on the indicating electrode. Organics which adsorb strongly produce a large response, while other organics that adsorb less produce a smaller response at the same concentration. Therefore, the total response to a mixture of organic solutes is a general indication of the organic content of the water.

Besides the general nature of its response, the EOC Analyzer is similar to conductivity monitors in other ways. The EOC Analyzer is simple to operate because it is highly automated. A goal of the development is automated, unattended operation for up to 30 days. The simplicity of the EOC measurement suggests that the EOC Analyzer ultimately will be a low cost instrument and will be inexpensive to operate and maintain.

The EOC Analyzer has one feature which is unlike conductivity or other organic solute monitors. The operating parameters of the EOC Analyzer can be adjusted to result in selective response to certain groups of organic solutes. This is achieved by the adjustment of electrochemical parameters and the electrolyte used for the measurement. Using this approach, the EOC Analyzer may be useful in providing additional information about the composition of effluents and wastewaters. It also can be used to monitor organic contaminants that are special indicators of water quality or treatment efficiency.

Objective

The objective of contract DAMD17-79-C-9058 was to identify and evaluate new applications for the EOC Analyzer. One application for which the EOC Analyzer was experimentally evaluated is the control of polyelectrolyte addition for particulate filtration in the ROWPU developed by the U.S. Army Mobility Equipment Research and Development Command (MERADCOM).

The objectives of this contract were achieved by surveying Army requirements for organic solute monitoring in water and wastewater treatment applications.

The ROWPU application was evaluated by assembling a test setup simulating the operation of the filter and polyelectrolyte addition portion of the ROWPU, and evaluating the response of the EOC Analyzer to filtrates treated with varying doses of polyelectrolyte. In this evaluation, the performance of the EOC Analyzer was compared to that of an on-line turbidimeter, which is a more traditional technique for monitoring polyelectrolyte addition.

Definitions

The organic solute concentration indices related to the EOC Analyzer are defined below:

1. Biochemical Oxygen Demand (BOD): BOD refers to the oxygen demand of wastewater that would result from microbiological activity, and is usually measured over a five-day period (referred to as BOD_5). BOD is expressed as mg/l.[7]

2. Chemical Oxygen Demand (COD): COD values represent the oxygen equivalents consumed in the chemical oxidation of oxidizable solutes (primarily organic species). The COD of the sample is determined by measuring the quantity of a strong chemical oxidizing agent consumed during oxidation of the solutes. COD is expressed as mg/l.[8]

3. Electrochemical Organic Content (EOC): EOC values refer to the measured response of the EOC Analyzer to organic solutes. The response of the Breadboard EOC Analyzer is reported in instrument units related to the indicating electrode interfacial capacitance.

4. Total Organic Carbon (TOC): TOC values represent the concentration of carbonaceous organic solutes in the sample, expressed in terms of milligrams of carbon per liter of sample.[7]

Program Organization

To evaluate the EOC Analyzer for new applications, the program was divided into the following tasks:

	1.0	EOC Applications Survey
	2.0	Evaluation of the EOC Analyzer and a turbidity montior for controlling polyelectrolyte addition in the ROWPU application
Deleted	3.0	Polyelectrolyte controller development

APPLICATIONS SURVEY

This section summarizes a survey that was performed to identify specific applications for which the EOC Analyzer could provide a capability in organic solute monitoring that does not now exist. The EOC Analyzer has been demonstrated to be especially responsive to large molecular weight and aromatic organics.[2] Therefore, only those applications have been included in which the water or wastewater contains aromatic or relatively high molecular weight organics. Furthermore, only applications have been selected that are expected to benefit through the use of a general indicator of organic concentrations, such as the EOC Analyzer. Applications which require measurements of specific

organic solutes are not included. That is, of the three broad categories of
environmental systems which have been described,[9] only the first two types
are considered here:

1. Systems that are relatively closed, i.e., there is some control of
    the entry of components into the system, and all components are well
    defined. An example is an output from a chemical plant that uses
    raw materials of known composition, processes them according to a
    particular procedure, and generates products and byproducts that are
    well defined.

2. Systems that are somewhat open in that entry of new components is
    possible but not frequent or likely, and components are somewhat
    defined.

3. Systems that are wide open to entry to almost anything at any time,
    and components are poorly defined.

Certain applications require, for regulatory purposes, the use of standard
methods such as the measurement of BOD or COD. It is recognized that the EOC
Analyzer is not a standard method and cannot replace these measurements.
However, the standard organic measurements are often too slow for process
monitoring and control applications. The operator requires timely information
regarding impending process changes and the efficiency of the process. If a
well established relationship exists between the EOC value and the standard
method, the EOC Analyzer can be used to control the process to maintain organic
concentrations at acceptable levels, as measured with the standard methods.

Other characteristics required in a water quality monitor for it to be success-
fully used in process control and monitoring applications are:[10]

1. Capability of measuring a representative sample.
2. Reliability of measurement.
3. Speed of measurement.
4. Simplicity of operation.
5. Low frequency of maintenance.
6. Acceptable capital and operating costs.

The Breadboard EOC Analyzer has demonstrated that the EOC concept has the
potential for satisfying those six requirements. The correlation of EOC
values with standard methods, if required, must be done as an application-to-
application basis. The specific requirements of each application also impact
the configuration, operator interfaces, packaging concepts and other design
features. Therefore, the applications in which the EOC Analyzer will be used
must be defined before more advanced versions are developed. Identification
of candidate applications began with an identification of Army environmental
requirements.

Army Environmental Requirements Related to the EOC Analyzer

The Department of the Army conforms to wastewater discharge regulations of the
U.S. Environmental Protection Agency (EPA), and drinking water standards
determined by the U.S. Public Health Service (PHS) and the EPA, as interpreted

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by the Surgeon General (TSG) of the Army.[11] The Chief of Engineers has primary Army Staff responsibility for coordinating and directing environmental activities, and has the responsibility of ensuring that environmental research and development projects support the Army's environmental program. The Surgeon General has the responsibility of monitoring, evaluating and disseminating health effects information related to environmental pollution, and providing technical assistance to the Office of the Chief of Engineers. Major Army commanders have the responsibility of establishing organizations to plan, execute and monitor the environmental programs within their commands.[11]

The Army is required to obtain National Pollution Discharge Elimination System (NPDES) permits from the EPA in accordance with the Federal Water Pollution Control Act, which covers the point source discharge of wastewater.[11] Many of these wastewaters produced by Army fixed and mobile installations are of types that are not unique to the Army (e.g., domestic wastewater effluents). However, other wastewaters contain Army-specific pollutants which may require special wastewater treatment processes to comply with NPDES regulations. Wastewater applications within this category, compatible with use of the EOC Analyzer, are discussed below.

Army-Specific Wastewater Applications

Significant Army-specific waterborne organic pollutants that have a known toxicity potential are listed in Table 1.[15] These compounds are explosives or the byproducts of munitions manufacturing. Therefore, applications for the EOC Analyzer in monitoring munitions wastewater treatment were investigated.

Munitions Wastewater Treatment Applications

Discharge limitations of organic pollutants from explosive manufacturing plants are listed in Table 2.[14,15] Discharge limits for the Best Practical Control Technology Currently Available (BPCTCA), in force since 1977, and Best Available Technology Economically Achieveable (BATEA), to be satisfied by 1983, are shown. Although the present regulations address general organic measurements such as BOD and COD, the 1983 pollution abatement strategy will probably be required to meet more specific organic concentration limits. For example, some discharge requirements already specifically call for the removal of dinitrotoluene (DNT), cyclotrimethylene trinitroamine (RDX), cyclotetramethylene tetranitramine (HMX) and tetryl.[16] Trinitrotoluene (TNT) must be reduced to a concentration less than 1 mg/l.[16] Table 3 lists the NPDES requirements for five Army ammunition plants and the typical composition of munitions wastewaters is listed in Table 4.[16]

Explosives and munitions manufacturing byproducts are large molecular weight organics with considerable aromaticity. The EOC Analyzer can be expected to detect these organics in highly treated wastewaters. Therefore, the EOC Analyzer may be useful in wastewater treatment processes designed to remove explosives and munitions byproducts.

Activated carbon and synthetic adsorbents have been used successfully for the treatment of munitions wastewaters.[16,17] Figure 3 illustrates the use of the EOC Analyzer in a munitions wastewater treatment process to detect organic breakthrough in the adsorption columns. In this example, the adsorption columns contain synthetic adsorbents and are regenerated by acetone extraction

TABLE 1   ARMY SPECIFIC ORGANIC POLLUTANTS IN WATER

Nitroglycerin
2,4,6-trinitrotoluene
Nitroguanidine
Trinitroresorcinol
Tetracene
PETN
RDX
HMX
0-Nitrodiphenylamine
Glycerol-1,3-dinitrate
Glycerol-1-nitrate
Glycerol-2-nitrate
2,6-dinitrotoluene
2,4-dinitrotoluene
4-Amino-2,6-dinitrotoluene
2-Amino-4,6-dinitrotoluene
Glycerol-1,2-dinitrate
Cyclohexanone
Hexamine
SEX

TABLE 2 EPA EFFLUENT LIMITATIONS FOR MUNITIONS PLANTS

| | Limitation, kg/1000 kg Product | | | |
| | For Any 1 Day, Max. | | 30-Day Average, Max. | |
	BPCTCA	BATEA	BPCTCA	BATEA
Existing Sources				
COD	7.77	0.85	2.59	0.55
BOD_5	0.72	0.11	0.24	0.067
New Sources				
COD	3.6	0.85	2.3	0.55
BOD_5	0.35	0.11	0.23	0.067

TABLE 3 EXISTING NPDES PERMIT DATA FOR MUNITIONS PLANTS

Location	Contaminant	Allowable Discharge, mg/l	
		Average	Maximum
Iowa AAP[a]	TNT	0.5	1.0
	RDX	15.0	25.0
Joliet AAP	TNT	0.5	0.75
Radford AAP	TNT	0.5	0.75
Volunteer AAP	TNT	0.3	0.50
Milan AAP	TNT	-	1.0
	RDX	-	1.0

(a) AAP = Army Ammunition Plant

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TABLE 4   TYPICAL MUNITION WASTEWATER CHARACTERISTICS

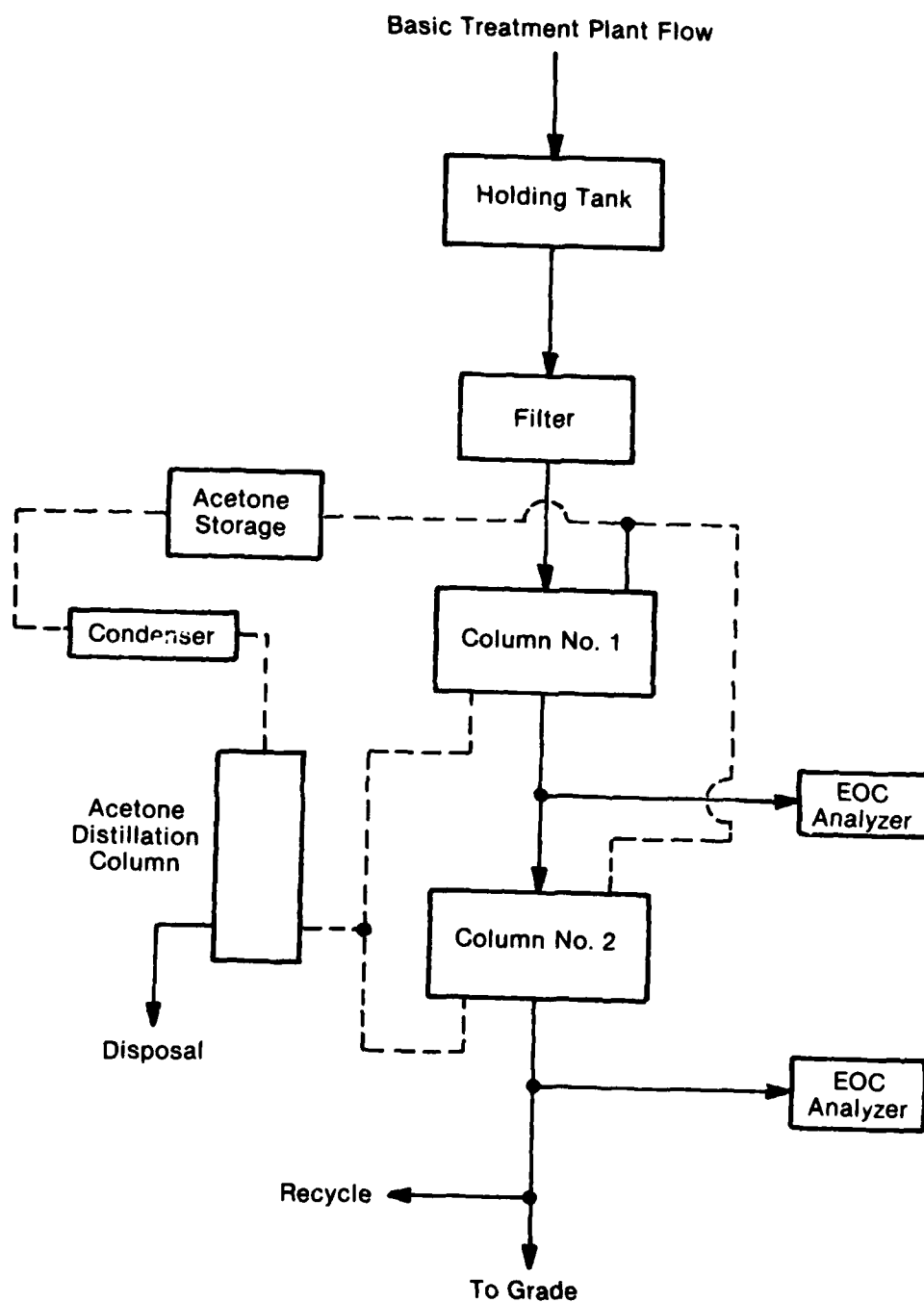| Parameters	Location		
	A	B	C
Flow Rate, GPD	20,000	100,000	1,000,000
Temperature, F	60 to 140	160	Ambient
pH	7	7	3.5
Organic Concentration, mg/l			
TNT	100 to 250	150 to 400	0 to 50
RDX	50 to 100	50 to 100	
DNT			0 to 20

FIGURE 3   MUNITIONS WASTE TREATMENT USING SYNTHETIC ADSORBENTS

with acetone recovery by distillation. Regeneration of the adsorption columns would be triggered by response of the EOC Analyzer to organic contaminants in the column effluents. When the regeneration was performed only when required, savings would result in labor, power for regeneration of the adsorbent and acetone distillation (in the case of the synthetic adsorbents). If activated carbon is used, power would be saved by reducing the frequency of the thermal carbon regeneration. The cost of replacing carbon expended in the regeneration would also be reduced.

Water Reuse Applications

The Department of the Army has announced a goal of utilizing water reuse where practical, and has announced a policy of establishing a leadership role in achieving the national goal of zero pollutant discharge.[11] As a result, water reuse has been evaluated for use in the approximately 135 fixed installations in the U.S. These consist of troop-oriented facilities (Training and Doctrine Command (TRADOC) and Forces Command (FORSCOM) posts) and depots.[18] This evaluation identified several major activities that could utilize treated wastewater, or which produce wastewater that could be reused in other activities after treatment. Table 5 lists several installations and water-related activities. The quality of wastewater produced from these activities is listed in Table 6, and the quality requirements for water used in these activities is listed in Table 7.[18]

Several of these activities, such as cooling water applications, do not involve organic removal in the treatment process, and therefore would not require the EOC Analyzer. Shower and laundry wastewater treatment does involve organic removal, but the EOC Analyzer has already been evaluated for this application and the results have been reported elsewhere.[6] Applications in which organic removal is required for the wastewater treatment, possibly requiring the EOC Analyzer for process monitoring and control, are shown in Table 8.[8] The major organic constituents of these wastewaters are also listed. Most of these organics are large molecular weight, aromatic organics. Therefore, it is reasonable to expect that the EOC Analyzer would respond to these organics, thereby being a useful indicator of organic contamination in effluents from processes utilized to treat these wastewaters. New reuse applications for which the EOC Analyzer may be employed are discussed below.

Wash Rack Applications

The Army has a large number of wash rack facilities for vehicle cleaning. Organic contaminants in the wash rack wastewaters primarily consist of oil and grease, detergents, some paints and solvents.

A specific application exists at Ft. Carson, Colorado where the U.S. Army Construction Engineering Research Laboratory (CERL) is evaluating modifications to wash rack facilities designed to meet the BOD and total suspended solids (TSS) discharge limits of 30 mg/l each for a 30-day average, and 45 mg/l for a 7-day average.[20] These discharge specifications further limit oil and grease concentrations to not more than 10 mg/l in any sample.

Figure 4 illustrates a waste treatment system designed for removal of oil and grease and reduction of BOD to acceptable levels.[20] Locations in the system

TABLE 5   PREVALENCE OF WATER-RELATED ACTIVITIES AT ARMY POSTS

Activities	Ft. Bliss	Corpus Christi A.D.	Ft. Carson	Ft. Campbell	Ft. Huachuca	Ft. Hood	Ft. Knox	Letter Kenny A.D.	Lex. Blue Grass A.D.	New Cumberland A.D.	Ft. Rucker	Sacramento A.D.	Ft. Sill	Tobyhanna A.D.	Toole A.D.
1. Aircraft Wash Rack		X	X	X	X	X				X	X		X		
2. Ash Handling				X			X		X					X	
3. Base Housing	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
4. Boilers	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
5. Cafeteria, Mess Halls, Restaurants	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
6. Cooling Tower	X	X		X	X	X	X	X	X	X	X	X	X	X	X
7. Dynamometer	X	X	X	X		X		X			X		X		X
8. Equip./Vehicle Maint. Shops	X	X	X	X	X	X	X	X		X	X	X	X	X	X
9. Fire Protection/Spill Washdown Reservoir	X		X	X	X	X	X	X		X	X			X	
10. Golf Course	X	X	X	X	X	X	X	X	X	X	X	X	X		
11. Hospital			X	X	X	X	X				X		X		
12. Industrial Laundry		X	X	X	X		X				X		X		X
13. Ind. Waste Trt. Plant		X	X	X			X	X				X			
14. Irrigation	X	X	X				X	X			X	X	X		X
15. Laundromats	X		X	X	X	X	X				X				
16. Metal Finishing/Plating		X	X	X			X	X			X		X	X	
17. Metal Cleaning		X	X	X		X	X	X		X	X	X	X		X
18. Motor Pool	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
19. Nondestructive testing		X	X			X	X	X	X	X	X	X	X	X	X
20. Paint Booths	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
21. Photography Labs.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
22. Recreational Lake			X	X	X	X	X	X		X	X	X	X	X	
23. Sewage Trt. Plant	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
24. Steam Cleaning		X	X	X	X	X	X			X	X	X	X	X	X
25. Swimming Pool	X	X	X	X	X	X	X	X	X	X	X	X	X		X
26. Vehicle Wash Rack	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
27. Water Treatment Plan		X		X	X		X	X	X		X				
28. Wet Scrubbers (Air Pollution														X	

TABLE 6   SOURCES OF RECLAIMED WATER – TYPICAL EFFLUENT QUALITY

Concentration (mg/l)

Constituent	Base Housing(a)	Hospitals/ Clinics	Industrial Laundries	Laundromats	Boilers	Cooling Waters(c)	Air Pollution Wet Scrubbers	Vehicle Wash Racks	Aircraft Wash Racks	Steam Cleaning	Metal Cleaning(d)	Paint Booths	Photographic Laboratories
BOD	200	250	450	200	5.0	7.0	10	60	5,700	1,300	3,000	8,100	300
COD	300	850	2,000	400	15	35	720	900	8,400	2,800		13,600	500
pH (pH units)		7.6	11.2	8.2	10.0	7.4	4.0			9.7	9.0		7.8
TDS	300+SWC(b)	1,400	2,000	360	3,500	5xSWC	5,000						2,900
O&G	50-100	45	300	750	0.5		0.3	60	280	245	350	280	4.0
SS	300	200	1,000	130	50	30	3,270	2,000	470	1,000	300	2,800	225
Phenol	0.15	0.3			0.5	0-0.1	0.001	0.01	8.5	8.0	7.0	1.2	0.001
Ag													0.5
B	1.0+SWC				10		0.1	0.1	0.1			0.1	18
Ca		15						31					
$CaCO_3$	80+SWC		740	250	50		200						
Cd		0.2	0.04		0.005								
Cr		1.1	0.06		3.0	0.05	0.01			0.5	0.5	13	
Cu	0.01		0.3		2.5	0.2	0.005	0.005	0.005	0.3		0.005	
Cl	100+SWC				1,000	5xSWC	400			0.2	25		4.8
Fe	1.0+SWC	0.3	1.0		2.5	0.6	5.3	4.7	1.1	0.01	0.6	3.2	2.0
K		34											
Mn								15					
Mg		16	6.4		2.5		72						
Na	50+SWC	360			1,000	5xSWC							
Ni					0-0.1			0.01					
NH_4	30		2.1		2.0	2.1	0.1	3.3	0.1	0.05		0.1	16
NO_3				1	150		28	33	0.8			28	8.8
P (Total)								2.5					
Pb	10	0.3	0.7		60					0.6	0.4		
PO_4,P		170	130	220	2.5		5.4	12	80	65	40	3.0	9.3
Si										2.0	6.0		
SO_4		35				5xSWC		2.9					
Zn			0.5		0-1								
Hardness (as $CaCO_3$)												4,900	
Detergents (as MBAS or ABS)		75		50	50						3.0		
Hexane Sol.				32									
Alk. as $CaCO_3$	50-150	125	500	182	500	5xSWC		115			400		
Level of Confidence(e)	1	1	1	1	1	1	3	1	2	1	1	2	1

(a) Applies to officers' quarters, BOQ, VOQ, barracks, and unclassified office space, as well as family housing.
(b) SWC = Source water concentration
(c) Recirculating type
(d) Rinse waters
(e) "Level of Confidence" denotes in data shown: 1 = High level of confidence. Well documented.
2 = Moderate level of confidence. Some documentation, some values may be engineering estimates.
3 = Low level of confidence. Limited documentation, most values are engineering estimates.

NOTE: Metal electroplating and finishing is a potential source of reclaimed water. The effluent contains high concentrations of various metal ions and cyanides, depending on the processes used, and small amounts of BOD, P, O&G, and SS.

TABLE 7   USERS OF RECLAIMED WATER – TOLERABLE WATER SUPPLY QUALITY

Concentration (mg/l)

Constituent	Laundries(a)	Recreational Lakes(b)	Fire Protection/ Spill Washdown Reservoirs	Irrigation(c)	Boilers	Cooling Waters(d)	Wet Scrubbers	Wash Racks and Steam Cleaning(e)	Metal Electro- plating and Finishing	Metal Cleaning	Paint Booths	Photographic Laboratories
BOD	45	10	10	30	1.0		100	10	1	1	30	0.1
COD	500	60	22	60	3.0	75	200	25	3	3	60	1.0
pH (in pH units)	6.0-6.8	5.0-9.0	5.0-9.0	4.5-9.0	9.0							
TDS	3,300	2,000		2,000	2,000	500-1,500	2,000	2,000	500	500		700
O&G	10	5	1.0	30	0.0		50	5			30	0.2
SS	30	10	10	50	10	100	100	10			60	1.0
Phenol	0.05	0.01	0.01	0.5	0.1		2.0	2.0	1	1		0.001
As	0.5								0.001	0.001		
B		0.1	0.1	3	2.0				0.05	0.05		0.1
CaCO$_3$					20		300	500	1.0	1.0		400
Cd				0.01								
Cr	0.5	0.1	0.1		0.5		0.5	0.5	0.1	0.1	0.5	0.5
Cu	1.0								0.05	0.05		0.01
Cn$^-$	0.2								1.00	1.00		
Cl		300		350	200	500	600	600	0.2	0.2		200
Fe	1.0	5.0	5.0	10	0.5	0.5	20	40	0.3	0.3		0.3
Mn	1.0			0.5	0.5				0.05	0.05		0.5
Mg		250		350	200		200					
Na		0.1	10	20	200		600	600	0.5	0.5	15	100
NH$_3$							20	5				
NH$_3$-N	1.5	2.5			2.5							0.1
NO$_3$			5.0				50		10	10		
Pb	0.5					0.3		1	0.05	0.05		20
PO$_4$-P		0.3	1		0.3							
Si					50	50						3.0
SO$_4$					200							
Zn	0.5								5.0	5.0		
Hardness (as CaCO$_3$)	50				10	50			10	10		
Alk. (as CaCO$_3$)	60				100	350						
DO	0	5		0	0	0		0	0			
Median coliforms (No./100 ml)	2.2	2.2	3		(f)			1.1				
Level of Confidence(e)	1	1	2	1	1	1	3	3	1	1	3	3

(a) Applies to both industrial laundries and coin-operated laundromats.

(b) Limited body contact

(c) Note that some plants are much less tolerant than others to various constituent concentrations and may require water of high quality from that shown in the Table. BOD, TDS, chlorides, and boron are particularly important in this regard.

(d) Applies to cooling waters for boilers, dynamometers, air compressors, vapor degreasers, and any operation that has a cooling tower.

(e) Rinse waters

TABLE 8   CONSTITUENTS OF SELECTED WASTEWATERS FOR REUSE

| Water Use	Constituents
Showers and Swimming Pools	Soap Disinfectant Insect Repellants Scouring Compounds Trace Human Wastes
Laundries	Detergents Solvents Trace Human Wastes
Wash racks and Industrial Uses	Oil and Grease Detergents Paints Solvents Heavy Metals Phenol Chlorinated Hydrocarbons Cyanide

Irrigation	Chemical and Biological
	    Components from Domestic
	    and Industrial Waste
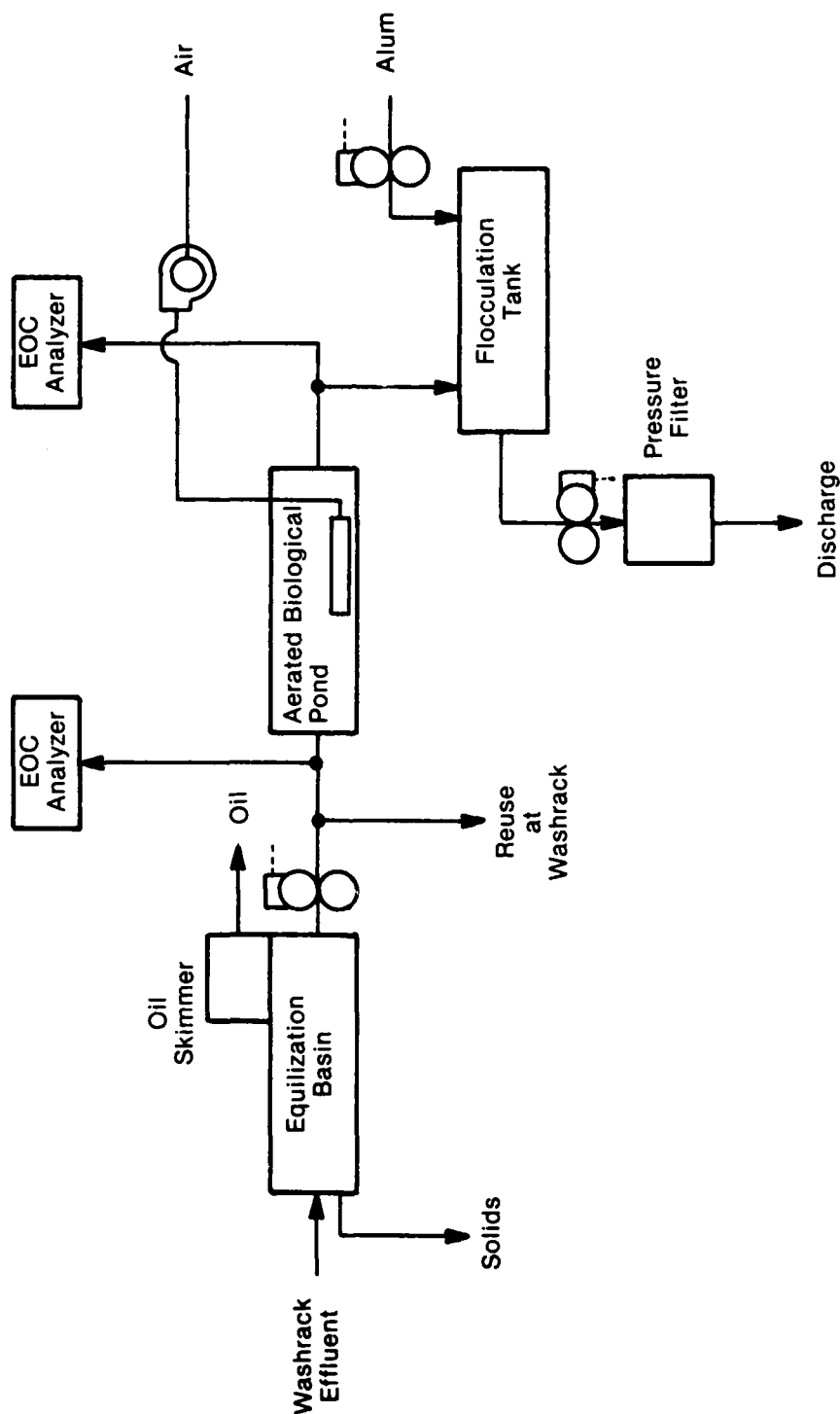
FIGURE 4 TREATMENT SCHEME FOR WASH RACK WASTEWATER TREATMENT

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where the EOC Analyzer could be utilized are also indicated. The Analyzer could be utilized to monitor the performance of the oil skimmer in the equalization basin, while providing a feed-forward indication of organic loading entering the biological pond. Effluent from the pond would be monitored to check performance and to detect upsets.

Figure 5 illustrates an oil and grease removal system based on dissolved air flotation.[21] In this system, the EOC Analyzer could be used to monitor the influent to the air flotation units for accurate control of the process, reducing power consumption during periods of low loading. The EOC Analyzer at the outlet of the dissolved air flotation system would record effluent quality and detect process failures.

Electroplating and Metal Finishing Applications

The evaluation of Army applications for water reuse identified Army electroplating and metal finishing facilities as a potential application of water reuse in the form of internal recycling of rinse water. Parts removed from the metal plating and finishing baths are rinsed to remove the plating bath chemicals. Primary environmental concern about the discharge of rinse waters centers about the cyanide (CN^-) and heavy metal ions in the water. However, organic contaminants also exist, and organics commonly used in the metal finishing industry are listed in Table 9.[22] Many of these organics are aromatic and most have a relatively high molecular weight.

Heavy metals and CN^- are removed from the rinse water using ion exchange. These organics can interfere by fouling the ion exchange resin, reducing its capacity to remove the CN^- and metals. To protect the anion and cation exchange resins, carbon adsorption columns are used to remove the organics (Figure 6).[23] In this application the EOC would detect breakthrough of the organics when the carbon is expended. Costs would be minimized by avoiding premature carbon replacement, while also avoiding the cost of replacing the ion exchange resin because of organic fouling.

Other Reuse Applications

The survey of water reuse applications identified several potential uses for treated wastewaters: (a) wash racks, (b) air pollution scrubbers, (c) cooling water makeup, (d) fire protection/spill washdown reserviors, (e) cleaning facilities and (f) steam cleaning.[18] It was determined that each of these applications could use secondary treated wastewater if it was further treated by, at a minimum, filtration and disinfection.

Most Army posts provide secondary treatment with trickling filters for organic removal.[18] Like other forms of biological treatment, the performance of trickling filters is dependent upon maintaining proper hydraulic and organic loading in the filter influent.[25] Periods of high organic loading can result in unacceptable organic concentrations in the effluent, while normal biological activity can be degraded during long periods of very low organic loading. Filter performance can be controlled by varying the recycle rate or by utilizing equalization ahead of the primary clarifier (Figure 7).[25]
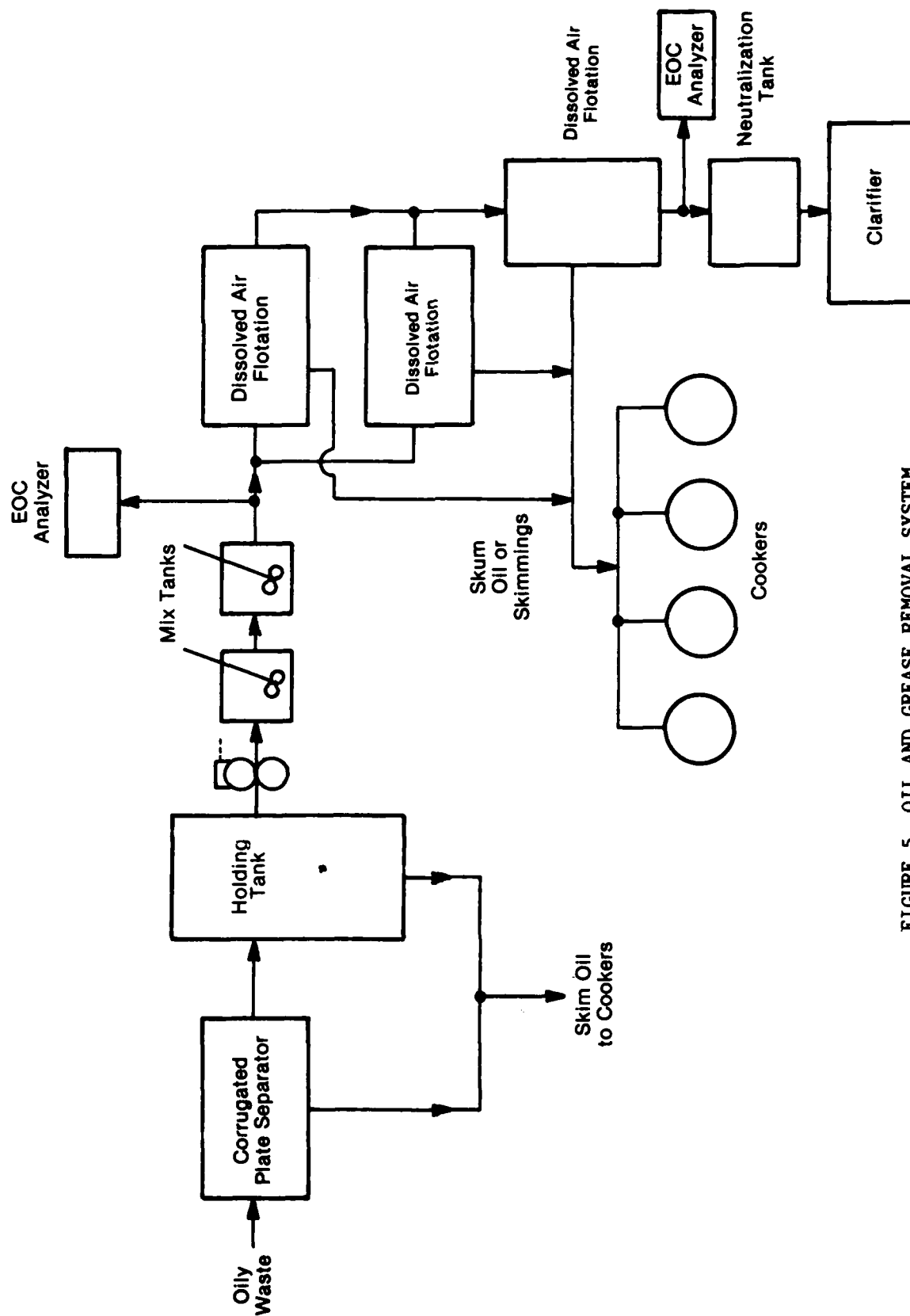
24

FIGURE 5   OIL AND GREASE REMOVAL SYSTEM

TABLE 9 ORGANIC POLLUTANTS IN THE METAL FINISHING INDUSTRY

Ammonium Citrate
Anisic Aldehyde
Antimony Potassium Citrate
Benzene
Citric Acid
Formaldehyde
Glue
Glycerine
Hydroxyacetic Acid
Isopropanol
Lard Oil
Methanol
Oxalic Acid
Potassium Citrate
Sodium Citrate
Sodium Gluconate
Stearic Acid
Sulfamic Acid
Tallow Glyceride
Tartaric Acid
Toluene
Trichloroethylene
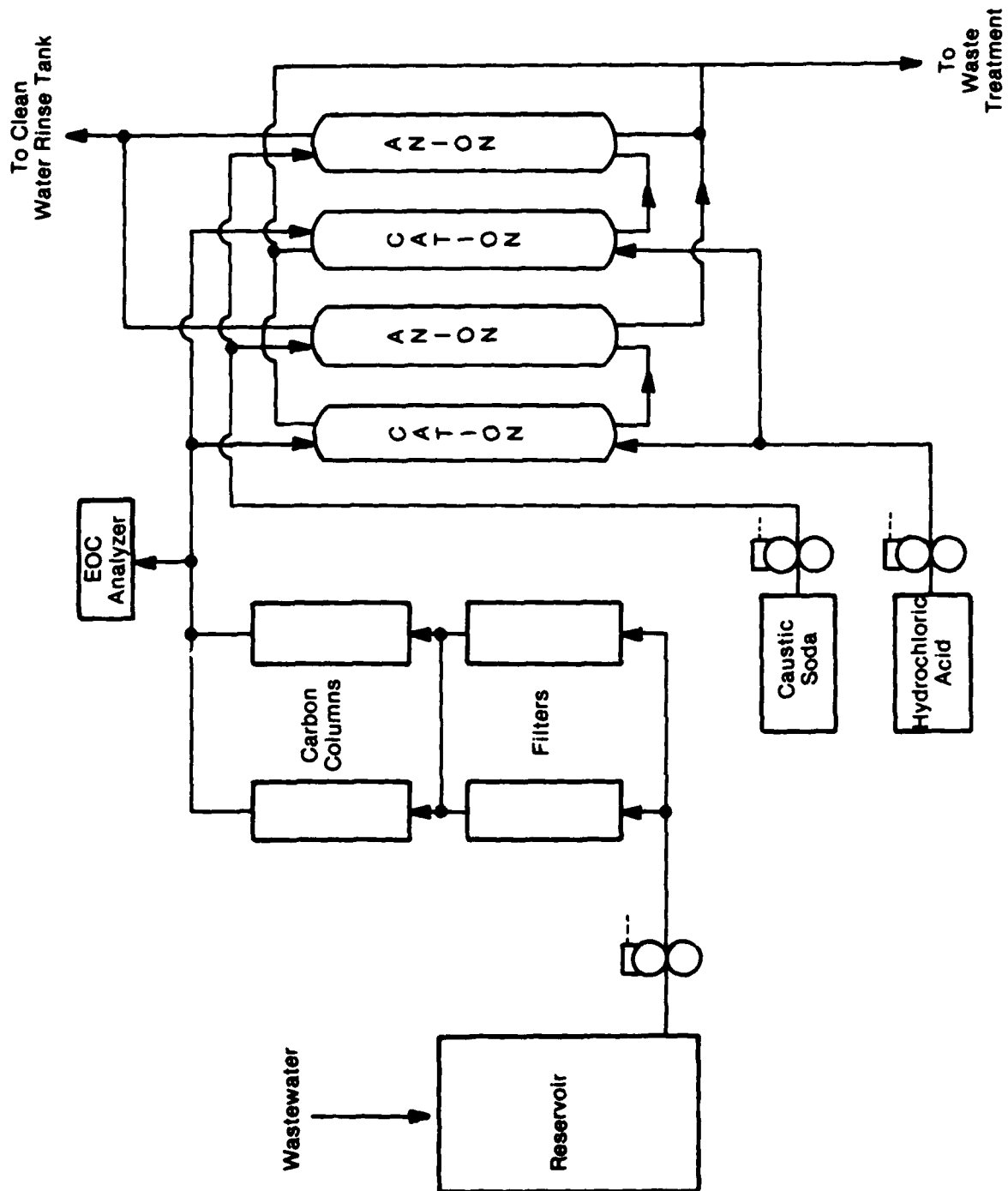Trichloroethane
Xylene

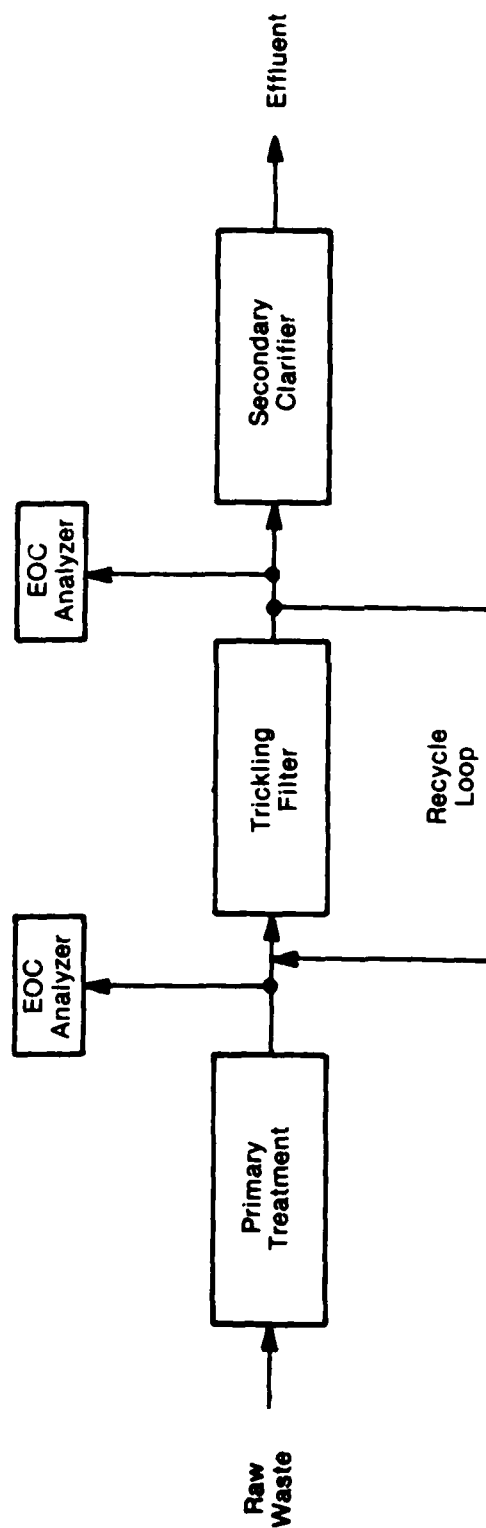FIGURE 6 METAL PLATING RINSE WATER REUSE SYSTEM BASED ON ION-EXCHANGE

FIGURE 7 SCHEMATIC OF TRICKLING FILTER TREATMENT SYSTEM

The EOC Analyzer probably can be used to monitor both the influent organic loading and the effluent quality. Most of the 56 organics identified among 150 detected organics in primary domestic sewage have a relatively high molecular weight and many are aromatic (Table 10).[26] These are the types of organics to which the EOC Analyzer can be expected to respond.

Secondary effluents from trickling filters and other biological treatment processes have been analyzed and major catagories of organic solutes have been identified (Table 11).[27] These types of organics also can be expected to produce significant responses, thereby allowing the EOC Analyzer to be used to monitor the organic loading of the filter effluent.

With the capability of monitoring both influents and effluents, the EOC Analyzer could be used to optimize the performance of a trickling filter by allowing the recycle rate to be controlled with respect to the influent and effluent organic loading.

<center>Wastewater Applications that are Not Army-Specific</center>

Biological Wastewater Treatment Application

Besides monitoring the performance of trickling filters, the EOC Analyzer may be useful in monitoring other types of biological processes. The most efficient of these is the activated sludge process, in which organic solutes are consumed by microorganisms contained in a sludge blanket within a large contactor. The sludge is withdrawn from the contactor, and a portion is returned to the contactor to maintain the necessary biological activity, while the excess is discharged (Figure 8). An excess will result from the multiplication of microorganisms in the contactor.

As effluent quality requirements become more stringent, the use of activated sludge plants within the Army may increase. However, the potential advantage of more efficient organic removal is of no value if it is not possible to control the process to routinely maintain this efficiency.

Manual operation of activated sludge plants has been demonstrated and has provided satisfactory effluents.[28] However, manual operation is limited by the expertise and reliability of the operators, and the procedures are affected by idiosyncrasies of the plant itself.[28,29] This fact was illustrated in a comprehensive survey of 287 biological wastewater treatment plants.[30] The ten major causes of poor plant performance were identified:

1. Improper operator application of concepts and testing for process control.
2. Inadequate process control testing and sampling.
3. Severe fluctuations of flow rates, hydraulic overloading and influent dilution, leading to nonoptimum biological conditions and even loss of solids from the final clarification stage.
4. Inadequate staff understanding of wastewater treatment.
5. Improper technical guidance, including misinformation from authortative sources.
6. Inadequate sludge wasting capability.

<center>29</center>

TABLE 10   COMPONENTS OF PRIMARY DOMESTIC SEWAGE EFFLUENTS

Compound	Concentration, mg/l
Ethylene Glycol	3
Maltose	0.5
Galactose	-
Glucose	-
Glycerol	15 to 19
Galacitol	2
Erythritol	5
Urea	16 to 43
N'-Methyl-4-pyridone-3-carboxamide	10 to 14
Phenylalanine	50 to 90
Uracil	16 to 58
5-Acetylamino-6-amino-3-methyluracil	140
N'-Methyl-2-pyridone-5-carboxamide	20 to 25
Tyrosine	34
Thymine	9 to 28
Theobromine	-
7-Methylxanthine	2 to 90
Inosine	11 to 23
Hypoxanthine	12 to 42
Xanthine	2 to 70
Adenosine	13
1,7-Dimethylxanthine	-
3-Methylxanthine	-
Caffeine	10 to 46
Guanosine	4 to 50
2-Deoxyglyceric Acid	7
4-Hydroxybutyric Acid	-
3-Deoxyarabinohexanoic Acid	7
Quinic Acid	50
1-Methylxanthine	70
2-Deoxytetronic Acid	6
Glyceric Acid	5
4-Deoxytetronic Acid	6
3-Deoxyerythropentonic Acid	4
2,5-Dideoxypentonic Acid	6
3,4-Dideoxypentonic Acid	13
Ribonic Acid	4
Oxalic Acid	2
2-Hydroxyisobutyric Acid	4
Uric Acid	20
Palmitic Acid	6 to 12
Orotic Acid	2 to 5
Succinic Acid	24
Phenol	6 to 12
3-Hydroxyphenylhydracrylic Acid	10 to 22
Phenylacetic Acid	10

Table 10 - continued

Compound	Concentration, mg/l
4-Hydroxyphenylacetic Acid	16 to 190
Benzoic Acid	3
2-Hydroxybenzoic Acid	2 to 7
4-Hydroxybenzoic Acid	1
3-Hydroxybenzoic Acid	7 to 40
3-Hydroxyphenylpropionic Acid	6 to 20
Indican	1 to 2
3-Hydroxyindole	2
o-Phthalic Acid	200
p-Cresol	20 to 29

TABLE 11   DISTRIBUTION OF ORGANIC GROUPS IN SECONDARY EFFLUENTS

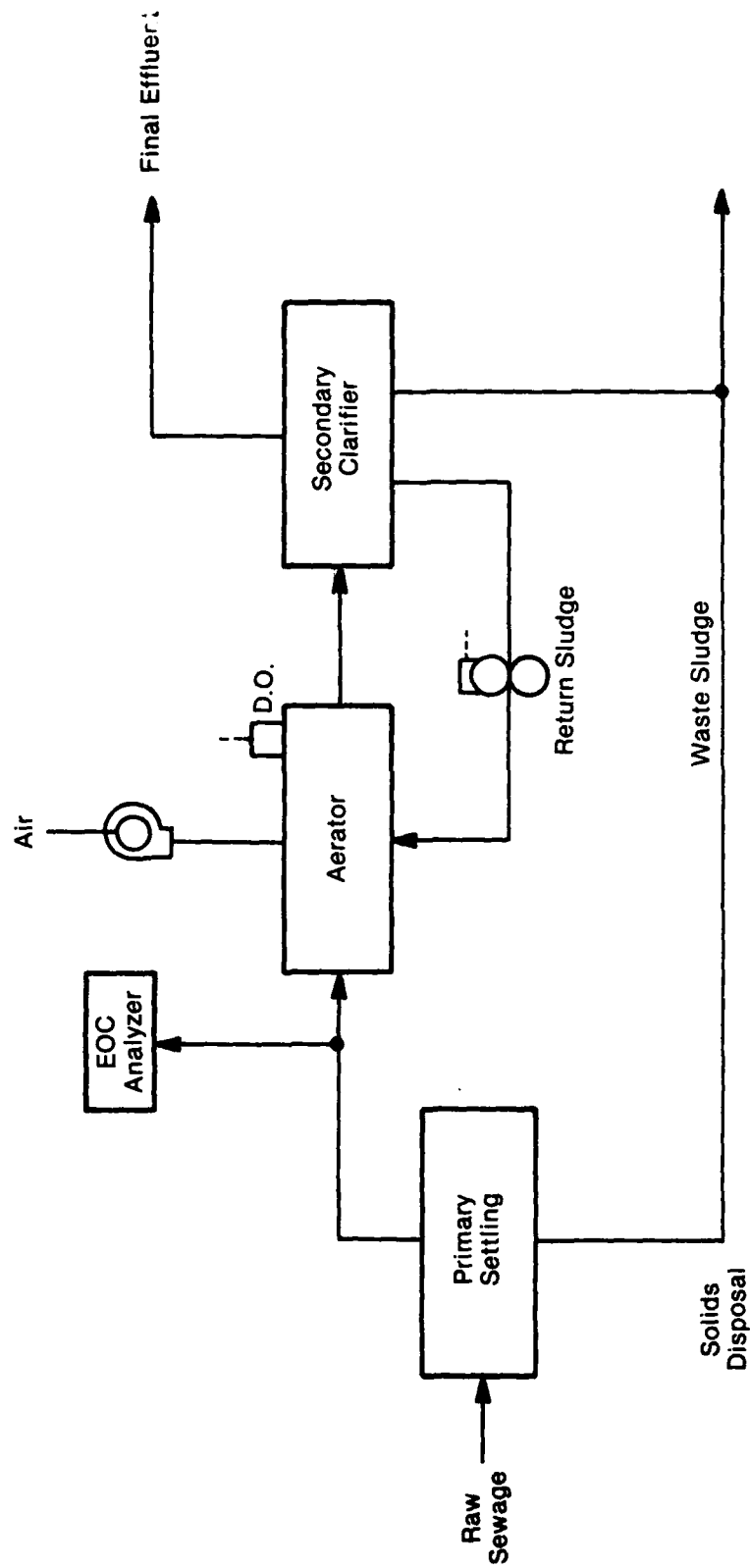| | Percent of Total COD | | |
Organic Groupings	Trickling Filter	Stabilization Pond	Activated Sludge
Proteins	21.6	21.1	23.1
Carbohydrates	5.9	7.8	4.6
Tannins and Lignins	1.3	2.1	1.0
Anionic Detergents	16.6	12.2	16.0
Ether Extractables	13.4	11.9	16.3
Fulvic Acid	25.4	26.6	24.0
Humic Acid	12.5	14.7	6.1
Hymathomelanic Acid	7.7	6.7	4.8

FIGURE 8   ACTIVATED SLUDGE PLANT WITH EOC ANALYZER CONTROL CAPABILITY

7. Lack of process controlability in parameters such as sludge return rates or trickling filter recirculation rates.
8. Lack of process flexiblity.
9. Ineffective operation and maintenance manual instructions.
10. Deficiencies in aerator design.

Deficiencies resulting from items 1, 2, 3, 4, 5, and 7 can be minimized through the use of process automation. For example, operating costs already have been reduced by controlling the activated sludge process on the basis of dissolved oxygen (DO) measurements to vary aeration rate.[30] A competitive control strategy is based on the ratio of Food-to-Microorganism (F/M) content.[25,30] The advantage of this technique is that during times of shock organic loading, a control strategy based on F/M content will maintain effluent standards.[30] The F/M strategy is based on the optimization of the sludge return rate to control the microorganism content in proportion to food entering the process. This requires an on-line organic analyzer to monitor the process influent to determine the food content. However, the lack of suitable on-line organic analyzers to date has limited the research into F/M strategies.[30]

The probable responsiveness of the EOC Analyzer to the organics in primary and secondary effluents has been discussed above. Therefore, the EOC Analyzer has the potential of providing the on-line measurement of the food content. The limitations in the use of other on-line analyzers (fouling by particulates and microbiological growth, plus complex and unreliable operation) can be addressed in the design of advanced versions of the EOC Analyzer.

Figure 8 shows the location of the EOC Analyzer for use in the F/M control strategy. Table 12 is a list of Army installations and installations of other government agencies which contain wastewater treatment plants, and which are potential users of the EOC Analyzer.[31]

Other Applications

Carbon adsorption for removal of organic contaminants has been discussed above in relation to treating metal finishing wastes. Carbon adsorption is also used for removal of pesticides from industrial wastewaters, and for removal of organics in physical-chemical wastewater treatment systems.[32,33] The types of organics in domestic wastewater have already been shown to be compatible with monitoring by the EOC Analyzer. Pesticides, likewise, are large organics with aromatic character. In wastewaters in which pesticides exceed 0.1 to 0.5 mg/l TOC, it is expected that the EOC Analyzer could be used to detect their presence. Figure 9 shows the schematic of a physical-chemical treatment plant, with location of the EOC Analyzer for monitoring organics in the treated wastewater.

Water Treatment Applications

The Department of the Army is required to provide drinking water satisfying the quality standards of the PHS and EPA, as interpreted by TSG.[11] The maximum acceptable levels for specific organic contaminants in drinking water, as established by the EPA, are listed in Table 13.[34] In the future the EPA also plans to limit the concentration of trihalomethanes to 0.1 mg/l for water systems serving a population of greater than 75,000 people, and in which a

TABLE 12   GOVERNMENT INSTALLATIONS WITH WATER TREATMENT SYSTEMS

|	
Camp Pendleton, CA	Ft. Ritchie, MD
USN Radio Station, CA	Seneca Army Depot, NY
Elgin AFB, FL	Ft. Leavenworth, KS
Kansas National Guard, KS	NASA, Wallops Island, VA
Ft. Knox, KY	Kentucky Military Institute, KY
USN Ammunition Depot, NB	USN Propellant Plant, MD
Picatinny Arsenal, NJ	Barksdale AFB, Shreveport, LA
Marine Corps Base, Camp Lejeune, NC	Ft. Bragg, NC
USN Air Station, Willow Grove, PA	N.A.S., North Island, CA
Ft. Bliss, TX	Ft. Monmouth, NJ
Redstone Arsenal, AL	Ft. Eustis, VA
Ft. Fisher AFB, Kure Beach, NC	Ft. Collins, CO
Corps of Engineers, GA	Ft. Detrick, MD
U.S. Dept. of Agriculture, OK	USN Corpus Christi, TX
White Sands Missile Range, NM	V.A. Hospital, Fresno, CA
Yosemite National Park, CA	Cornhusker Ammunition Depot, NB
Ft. Sill, OK	Corps of Engineers, Washington, DC
Forrest Service, Ruidoso, NM	USN, Mayport, FL
N.A.S. Moffett Field, CA	Sierra Army Depot, Herlong, CA
Jefferson Proving Ground, IN	U.S. Penitentiary, Lewisburg, PA
Marine Corps Base, Twentynine Palms, CA	Hill AFB, UT
USN Air Facility, CA	V.A. Hospital, Fort Lyons, CO
N.A.S., Mirama, CA	Petersen Field AFB, CO
Ellsworth AFB, SD	Glenview Naval Air Station, IL
GSA, New Orleans, LA	Clinton-Sherman AFB, OK
Utah National Guard, UT	U.S. Coast Guard, VA (Portsmouth)
N.A.S., Lemoore, CA	Lexington-Blue Grass Army Depot, KY
USAF Military Academy, CO	State Correctional Institute, PA
Marine Corps Supply Center, GA	Savanna Army Depot, IL
Government of Guam	Sioux City AFB, IA
N.A.S., Meridian, MS	Naval Amphib. Base, VA
Pease AFB, NH	Ft. Polk, LA
USN Station, NY	Ft. Dix Officer's Mess, NJ
Lockbourne AFB, OH	Patrick AFB, FL
Ft. Hood, TX	McQuire AFB, NJ
USN Supply Center, VA	Kingsley Field, OR
Marine Corps Base, Quantico, VA	Federal Correctional Inst., FL
Cape Kennedy, FL	Letterkenny Army Depot, PA
Bureau of Reclamation, NY	Army Corps of Engineers, Ft. Stewart, GA
V.A. Hospital, Butler, PA	U.S. Dept. of Justice, KY
Veterans Administration, Gainesville, FL	R.C. AFB, Seven Islands, Quebec
Ellsworth AFB, SD	Ellsworth AFB, SD
Ft. Campbell, KY	Officer's Club, Willow Grove, PA
Kingsley Field, OR	San Francisco Bay Naval Shipyard,
Otis AFB, Falmouth, MA	Vallejo, CA
Eufala Nat'l. Wild Life Refuge, AL	Anniston Army Depot, AL
Wright-Patterson AFB, OH	Cannon AFB, NM
Camp Pickett, VA	U.S. Naval Weapons Labs, VA
Wheeler AFB, HI	Ft. Eustis, VA
Dept. of Correction, Lorton, VA	Ft. Leonard Wood, MO
Camp Shelby (Sewage Plant) MI	Griffiss AFB, NY
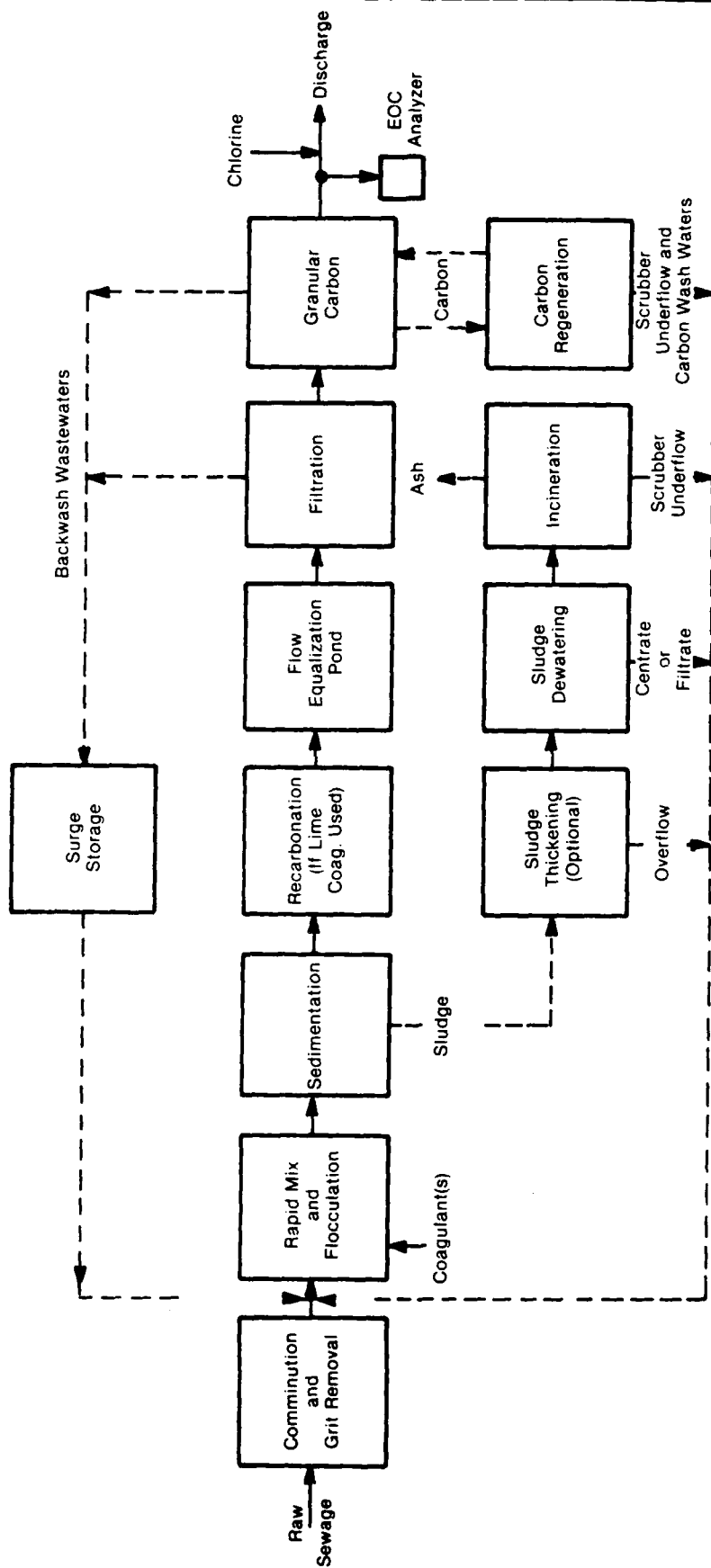
FIGURE 9   SCHEMATIC OF A PHYSICAL-CHEMICAL TREATMENT PLANT

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TABLE 13   MAXIMUM CONTAMINANT LEVELS FOR ORGANIC CHEMICALS

	Concentration, mg/l
Chlorinated Hydrocarbons:	
Endrin	0.0002
Lindane	0.004
Methoxychlor	0.1
Toxaphene	0.005
Chlorophenoxys:	
2,4-D	0.1
2,4,5-TP Silvex	0.01

disinfectant is added to the water as part of the treatment process.[35,36]
Water systems serving populations between 10,000 and 75,000 are required only
to monitor the level of total trihalomethanes in their systems for one year,
and water systems serving less than 10,000 people are not required to comply
with the regulation or conduct monitoring. Trihalomethanes are not strongly
adsorbed on the EOC Analyzer indicating electrode. Therefore, it is improbable
that they can be detected by the EOC Analyzer at the concentrations necessary
to ensure that drinking water quality specifications are met. The low concen-
trations of the toxic compounds listed in Table 13 are also lower than the
normal operating range of the EOC Analyzer. Although the chemicals in Table 13
fall into the categories of compounds to which the EOC Analyzer is responsive,
the low concentrations which can be expected in drinking water preclude the
use of the EOC Analyzer for monitoring them.

The EOC Analyzer may find application in the treatment of raw water to remove
the precursors of trihalomethane formation. It is known that trihalomethanes
are produced by the reaction of free chlorine with naturally occurring compounds
(principally fulvic and humic acids).[37] Methods are being evaluated in
which fulvic and humic acids are removed from the raw water prior to chlorination.
Coagulation, sedimentation and carbon adsorption have been shown to be effective
in the removal of fulvic and humic acids.[37] The EOC Analyzer is responsive
to these organics and can be used to monitor the removal efficiency of these
compounds prior to chlorination. In cases in which carbon adsorption is used
to remove the precursors, the EOC Analyzer can be used to monitor organic
breakthrough and trigger carbon regeneration.

EVALUATION OF EOC FOR POLYELECTROLYTE DOSAGE MONITORING

The potentially small size, simplicity, low cost and high automation of advanced
versions of the EOC Analyzer make it an attractive approach to organic solute
monitoring in transportable systems designed for field use. One such system
is the ROWPU, developed by MERADCOM.[38] This system purifies raw water by
removing suspended materials with a mixed-bed filter and a 5 mm polishing
filter (Figure 10). Dissolved solids are removed using reverse osmosis (RO).
The RO subsystem primarily will be used only when the raw water is brackish or
salty.

Polyelectrolyte is added to the raw water to coagulate colloidal particles,
improving filter performance. However, if the polyelectrolyte dosage is not
optimized, premature clogging of the polishing filter occurs, or mudballing
occurs in the mixed-media filter, making filter backwashing difficult. There-
fore, a means is required to determine the optimum polyelectrolyte dosage. To
date, the ROWPU has been operated with a fixed polyelectrolyte dosage, which
is not the optimum value for all waters.

The EOC Analyzer was evaluated because of its known responsiveness to many
large molecular weight organics. It was believed that the Analyzer would
respond both to the polyelectrolyte and to the naturally-occurring organics in
the water. It was anticipated that the EOC Analyzer would detect the optimum
polyelectrolyte dosage by determining the dose at which organic contaminants
in the filtrate were minimized by the most effective coagulation and filtration
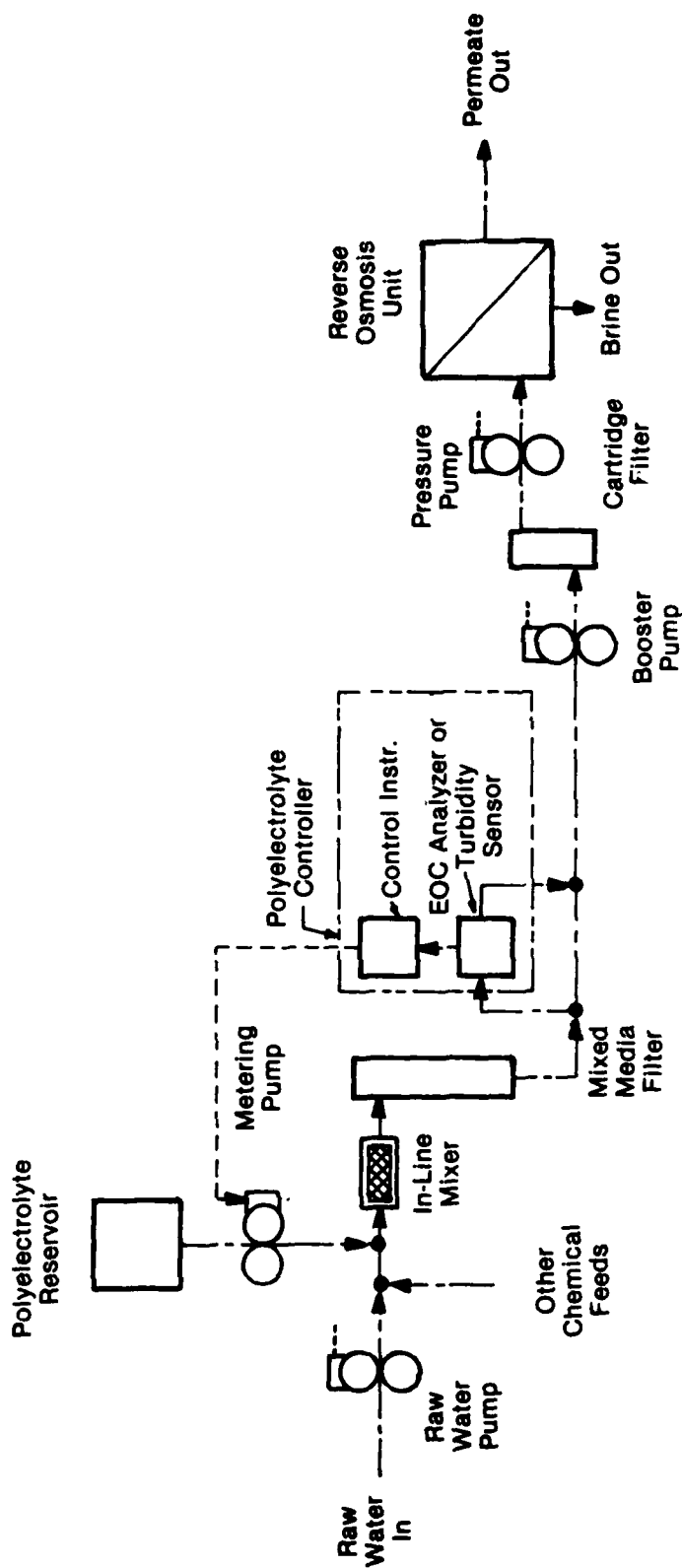conditions.

FIGURE 10 BASIC ROWPU BLOCK SCHEMATIC, SHOWING INSTALLATION
OF POLYELECTROLYTE CONTROLLER

During the evaluation, the filtrate was also monitored with on-line and labora-
tory turbidimeters, which are a common technique for monitoring filter performance.
The turbidimeters respond to the suspended particulates in the filtrate,
detecting optimum polyelectrolyte dosage by detecting minimum turbidity.

The EOC Analyzer and on-line turbidimeter were tested to compare response
sensitivities, drift and other analytical characteristics.

Initial Feasibility Tests

Initial feasibility tests were performed to demonstrate that the EOC Analyzer
was sensitive to the CAT-FLOC T-1 polyelectrolyte selected for use with the
ROWPU.[38] Preliminary Analyzer operating conditions were established and
response curves were determined for polyelectrolyte in distilled water. The
data in Figure 11 confirms the sensitivity of the EOC Analyzer for this substance.

Response Characterization Tests

The capabilities of the EOC Analyzer and turbidimeter to detect optimum dosages
of polyelectrolyte were subsequently tested.

<u>Test Methodology</u>

Test hardware, conditions and procedures were selected to simulate ROWPU
operating conditions. This methodology is elaborated below.

<u>Test Hardware and Procedures</u>. Water influents were treated with variable
dosages of polyelectrolyte, and were filtered and analyzed using the test
setup illustrated in Figure 12. The test instrumentation and conditions
employed during the experiments are listed in Tables 14 and 15.

A one-inch diameter mixed-media filter was assembled as recommended by MERADCOM.
The experimental influent flow rate was 100 cm^3/min (0.026 gal/min), correspond-
ing to a surface loading rate of approximately 0.27 m/min (6.5 gal min^{-2} ft^{-2})
as specified for the mixed-media filter in the 600 gal/h ROWPU[37] The filter
was periodically backwashed at 0.82 m/min (20 gal min^{-1} ft^{-2}) for at least 15
min, typically between each group of experiments.

Test waters were stirred in the influent reservoir during the experiments to
maintain homogenity. Each batch of natural water was analyzed for turbidity,
conductivity, pH, and chloride (Cl$^-$). The polyelectrolyte was injected at
controlled rates into the influent stream and was dispersed in a flash mixer
having a 15 second detention time. After flowing through the mixed-media filter,
the water was analyzed by the Breadboard EOC Analyzer, an off-line laboratory
turbidimeter and an on-line turbidimeter.

<u>Water Types</u>. Fresh water and salty water samples were tested. Fresh water
influents were selected to provide a spectrum of types that may ultimately be
treated by the ROWPU. The water sources selected are listed below:

- Well (LSI Well)
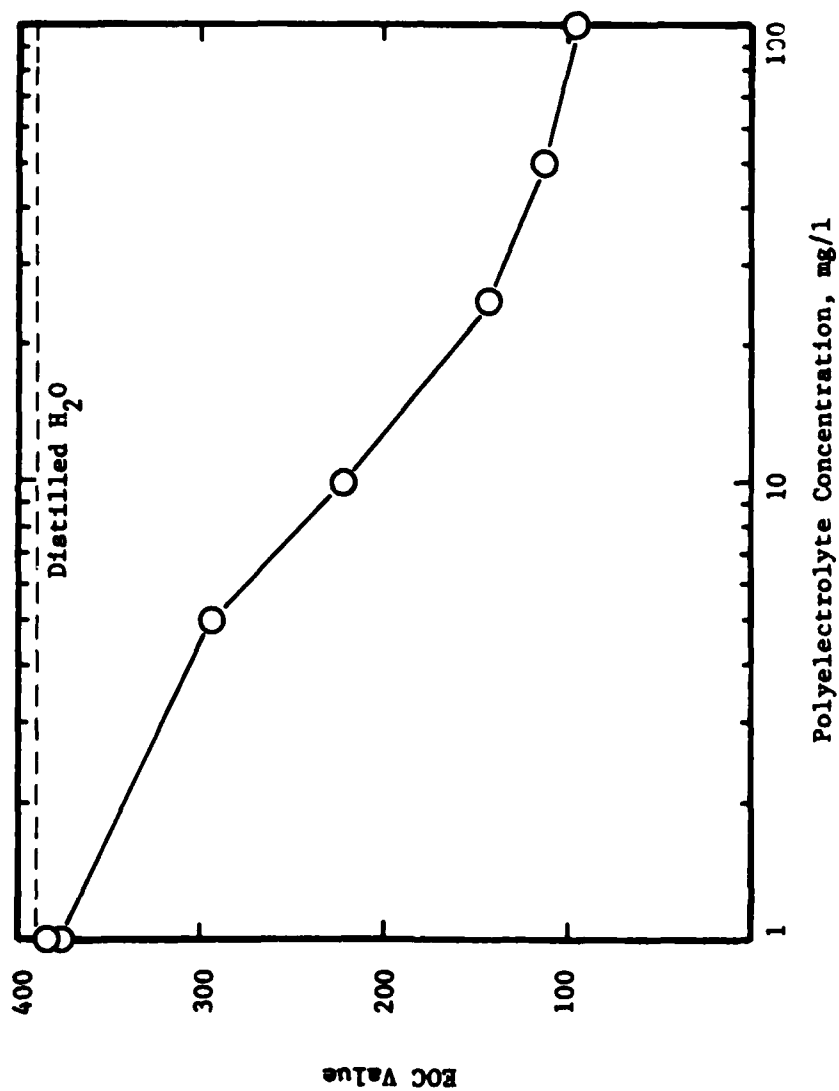- Lakes (Shadow Lake, Lake Forest and Lake Erie, sampled at Madison,
OH)

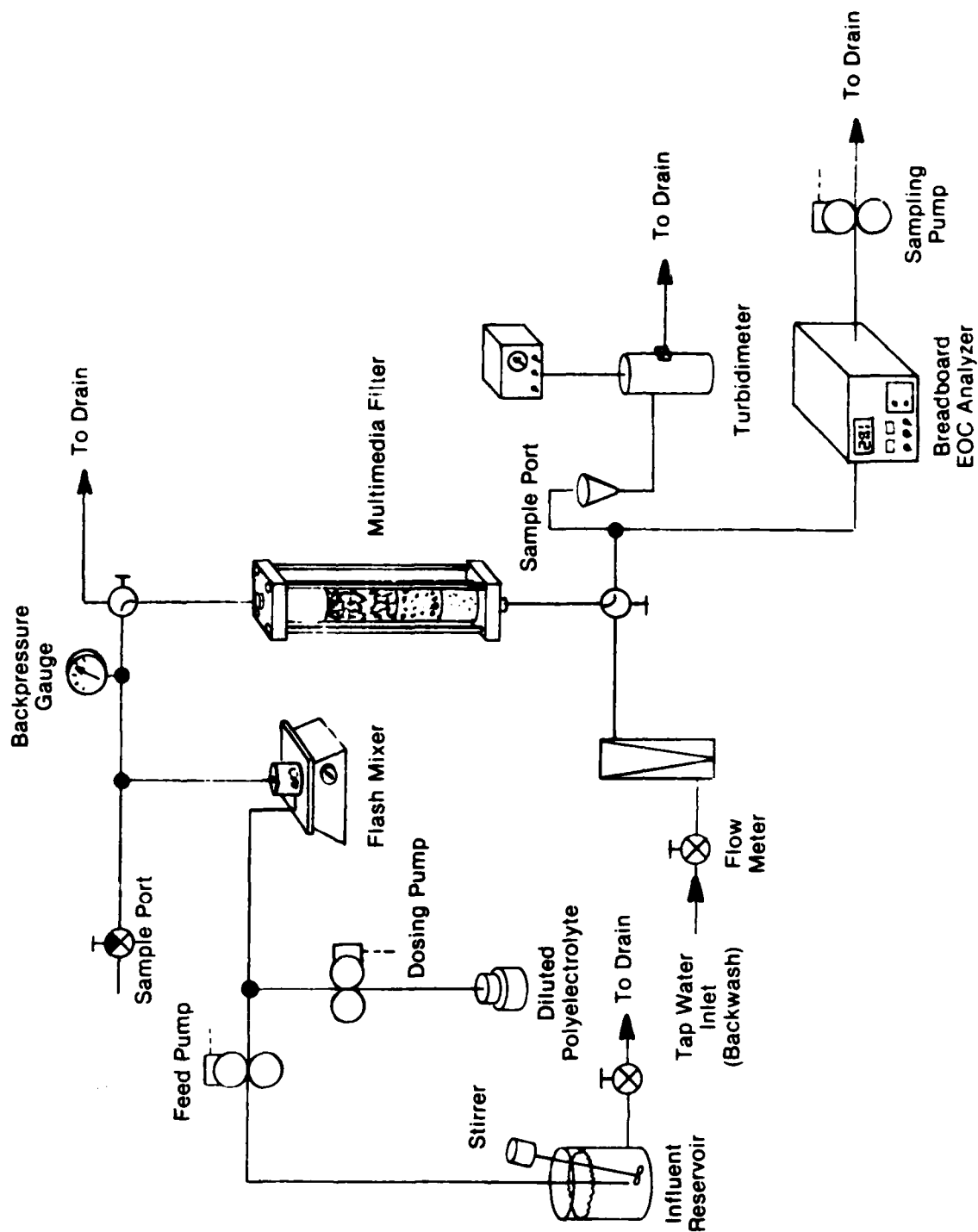FIGURE 11 EOC ANALYZER RESPONSE TO CAT-FLOC T-1 POLYELECTROLYTE

41

FIGURE 12 TEST SETUP

TABLE 14 ANALYSIS INSTRUMENTATION

Instrument	Description
EOC Analyzer	Life Systems Breadboard EOC Analyzer
Laboratory Turbidimeter	Hach Model 2100A
On-Line Turbidimeter	Hach 1720A Low Range Turbidimeter
Electrolytic Conductivity Meter	Beckman RC-19 Conductivity Bridge
pH Meter	Orion 601A Digital pH Meter
Chloride Analysis Kit	Lamotte Low Chloride Test Kit

TABLE 15   TEST CONDITIONS

Filter

    Type   Mixed-Media

    Bed Depths

        0.9 to 1 mm Anthracite, cm (in)   45.7 (18)

        0.45 to 0.55 mm Sand, cm (in)   22.8 (9)

        Fine Garnet, cm (in)   7.6 (3)

    Loading Rate, m/min (gal $min^{-1}ft^{-2}$)   0.27 (6.5)

    Backflush Rate, m/min (gal $min^{-1}ft^{-2}$)   0.82 (20)

Process Water Flow Rate, cm/min (gal/min)   100 (0.026)

Water Temperature   Laboratory Ambient

Polyelectrolyte

    Type   CAT-FLOC T-1

    Dosage Range, mg/l   0.2 to 10

- Creek (Tinkers Creek)
- Rivers (Cuyahoga River and Chagrin River)

Salty water samples were prepared by addition of salt to well water. A soil suspension was added to increase the turbidity of the well water, which was otherwise too clear for testing during the salty water tests.

Polyelectrolyte Dosages. The maximum allowable dosage of CAT-FLOC T-1 poly-electrolyte permitted by the EPA for treatment of potable water is 5 mg/l.[39] The polyelectrolyte dosages utilized in testing of a prototype ROWPU ranged from 2.5 to 8.8 mg/l.[40] Therefore, a polyelectrolyte dosage range of 0.2 to 10 mg/l was selected for these experiments.

EOC Analyzer Optimization

An optimization study was performed to obtain the best operating conditions for the instrument prior to determining the response characteristics of the Breadboard EOC Analyzer for a variety of natural waters.

The degree of adsorption of organic molecules on the indicating electrode of the EOC Analyzer is determined by the adsorption potential. This potential can be optimized somewhat for a particular organic species. The best polyelectrolyte adsorption potential was determined to be -0.6 V, based on the maximum decrease between EOC values for 0 and 5 mg/l polyelectrolyte solutions in distilled water, as shown in Figure 13. However, a slight increase in the EOC values between well waters with and without polyelectrolyte was observed. This was probably due to a high concentration of organic molecules in the well water, which not only overshadowed detection of the polyelectrolyte but possibly adsorbed to some extent on the large polyelectrolyte molecules, actually decreasing the EOC value of the water. This data provided a preliminary indication that the organic concentrations in natural waters may limit the usefulness of the EOC Analyzer, as presently implemented, for polyelectrolyte detection.

Some organic molecules are more difficult to clean off the indicating electrode between EOC measurements than others. An experiment was therefore performed to verify that the electrode was cleaned between polyelectrolyte measurements. The electrode cleaning potentials and cleaning periods projected to be adequate for polyelectrolyte dosage control applications were initially selected, based on prior experience. These conditions were then checked by alternately analyzing well water containing 5 mg/l of polyelectrolyte and distilled water to determine the reproducibility of the measurements. The results of this experiment, shown in Figure 14, verify that the electrode was cleaned effectively between measurements. If this was not the case, the EOC values for distilled water would have become successively smaller.

EOC/Turbidimeter Response Characterization

The performance of the EOC Analyzer and turbidimeter was evaluated in the following tests.

Fresh Water Tests. The relationships between polyelectrolyte dosage and EOC response and turbidity were determined for a variety of fresh water samples.
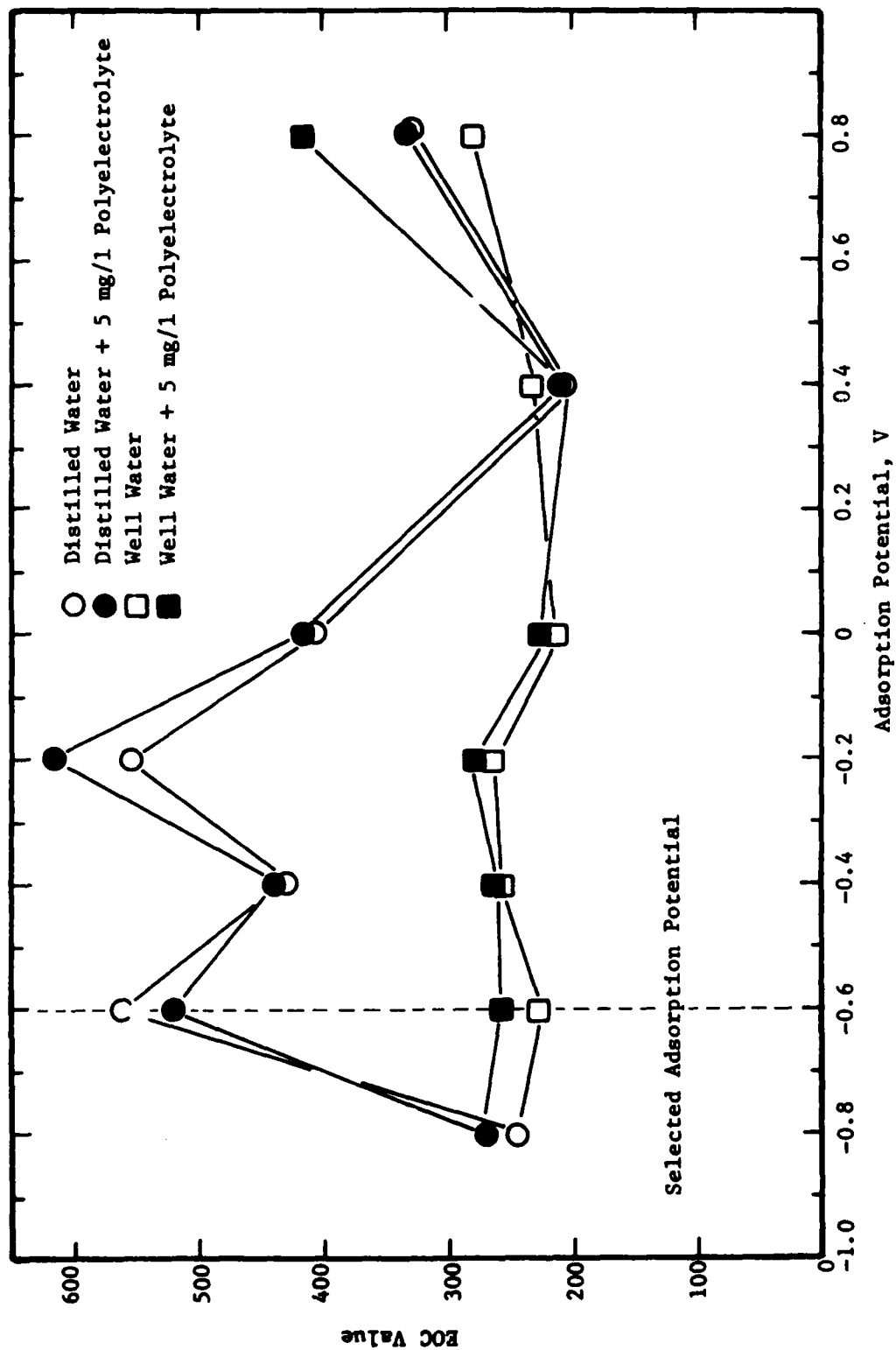
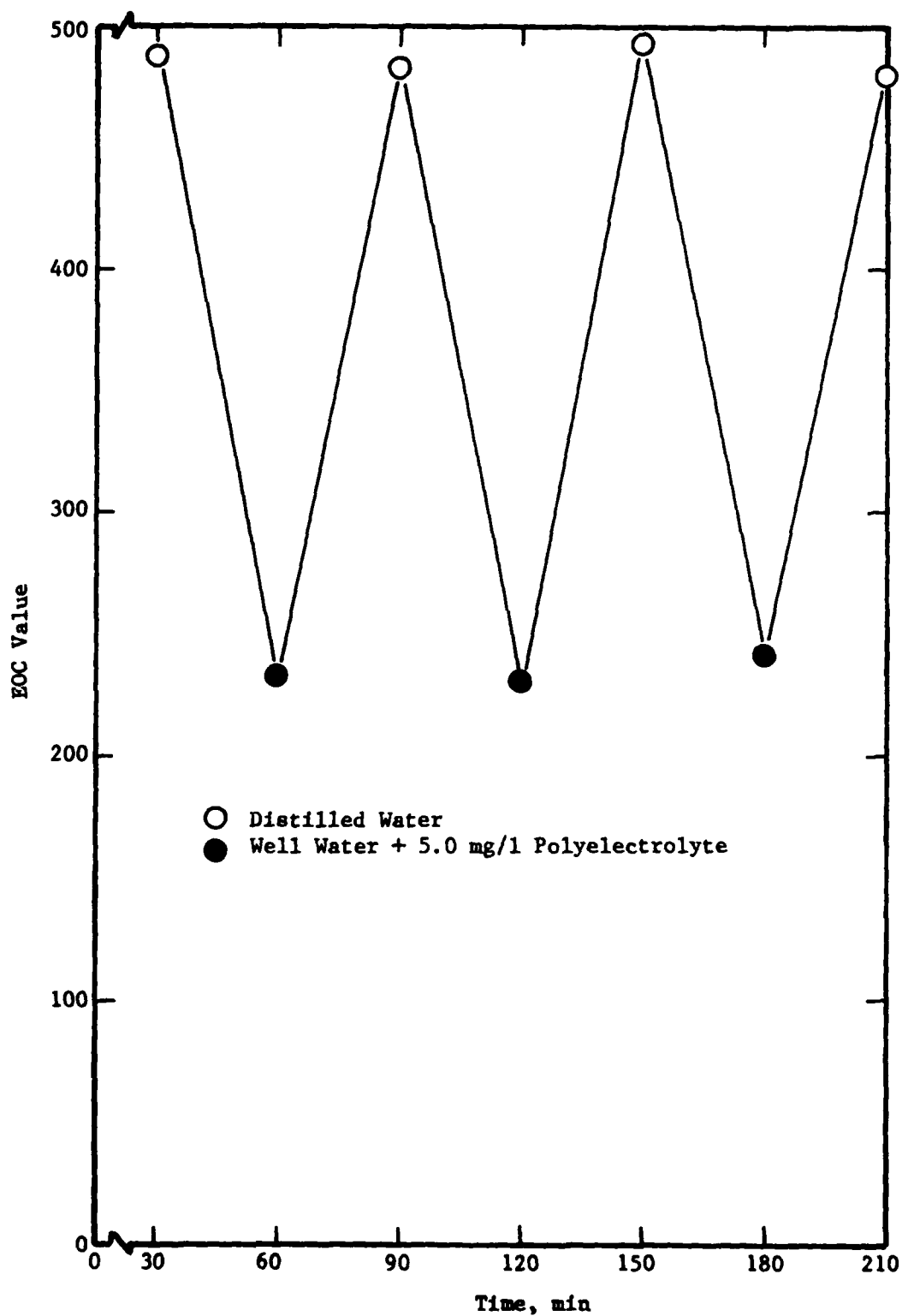FIGURE 13 RESULTS OF EOC ADSORPTION POTENTIAL OPTIMIZATION

FIGURE 14   RESULTS OF EOC ELECTRODE CLEANING CONDITIONS TEST

Life Systems. Inc.

The response versus dosage curves for the various waters are shown in Figures 15 and 16.

These data verify that turbidity is an effective means for determining correct polyelectrolyte dosages. Minimum turbidities, or turbidities approaching a minimum, were obtained at apparently optimum polyelectrolyte dosages. In most cases turbidities were less than 1 Nephelometric Turbidity Unit (NTU) at the proper polyelectrolyte dosage. Higher turbidities correlated in general with high influent turbidities, except for the water from Tinkers Creek, as shown in Figure 17. Even a 10 mg/l polyelectrolyte dosage was insufficient to reach a minimum turbidity with Tinkers Creek water.

The Breadboard EOC Analyzer, however, did not detect optimum polyelectrolyte dosages. It apparently responded so strongly to the organic contaminants already in the water that any response to the polyelectrolyte or removal of organics through coagulation and filtration was made insignificant. The response of the EOC Analyzer to the samples (Figure 16) correlates to the expected relative pollution levels in each water. Water collected from the Cuyahoga River after a heavy rain storm (black squares) produced larger EOC values (lower organic loading) than before the storm (open squares).

The turbidity data also shows how the quality of the water can vary with time and weather conditions. The first tests performed on water from the Cuyahoga River were performed with the flash mixer off, with a second experiment scheduled the next day with water from this river and the mixer on to test the effects of the mixer on filter performance. However, the rain prior to and during the collection of the second samples caused the influent turbidities to be extremely high (340 NTU). This exceeded the capacity of the mixed-media filter in the time required for the test. Filter breakthrough occurred, resulting in extremely high effluent turbidities.

Saltwater Tests. The ROWPU will be used to treat seawater and brackish water as well as fresh water. Seawater has a very high concentration of dissolved solids, principally sodium chloride (NaCl). Polyelectrolyte dosage curves were therefore obtained for a natural water containing different concentrations of salt to determine the effect of high Cl^- and high dissolved solids concentrations on the capability of a turbidimeter and the Breadboard EOC Analyzer to detect correct polyelectrolyte dosage.

Dosage curves were determined for 0, 200, 2000 and 20,000 mg/l Cl^- (as NaCl) to cover the salt concentration range of fresh and brackish water and seawater. A single water sample was used with successive additions of NaCl to attain desired Cl^- concentrations.

These dosage curves are plotted in Figure 18. The curves corresponding to all Cl^- concentrations except 20,000 mg/l have the conventional shape. Turbidities increased after the optimum dosage was obtained, although many of the dosage curves obtained in previous experiments had not reached a true minimum. No correlation between EOC and optimum dosage was observed.

Turbidities for samples having no polyelectrolyte decrease with increasing Cl^- content, except for those containing 20,000 mg/l Cl^-. This is probably due to the isoelectric, charge neutralizing effect of a high ionic solute concentration,
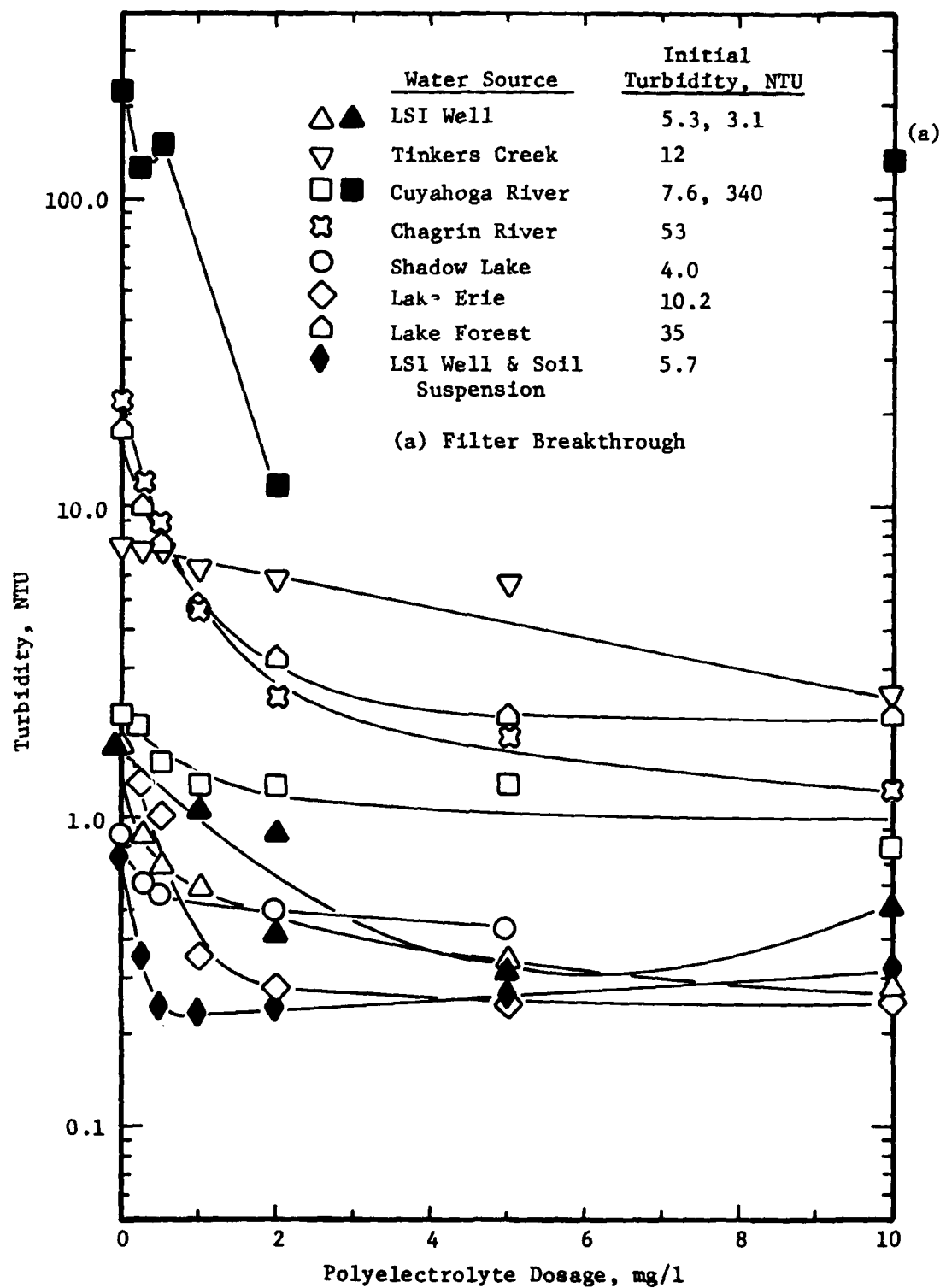
FIGURE 15   CLARIFICATION VERSUS POLYELECTROLYTE DOSAGE CURVES FOR NATURAL WATER FILTRATES
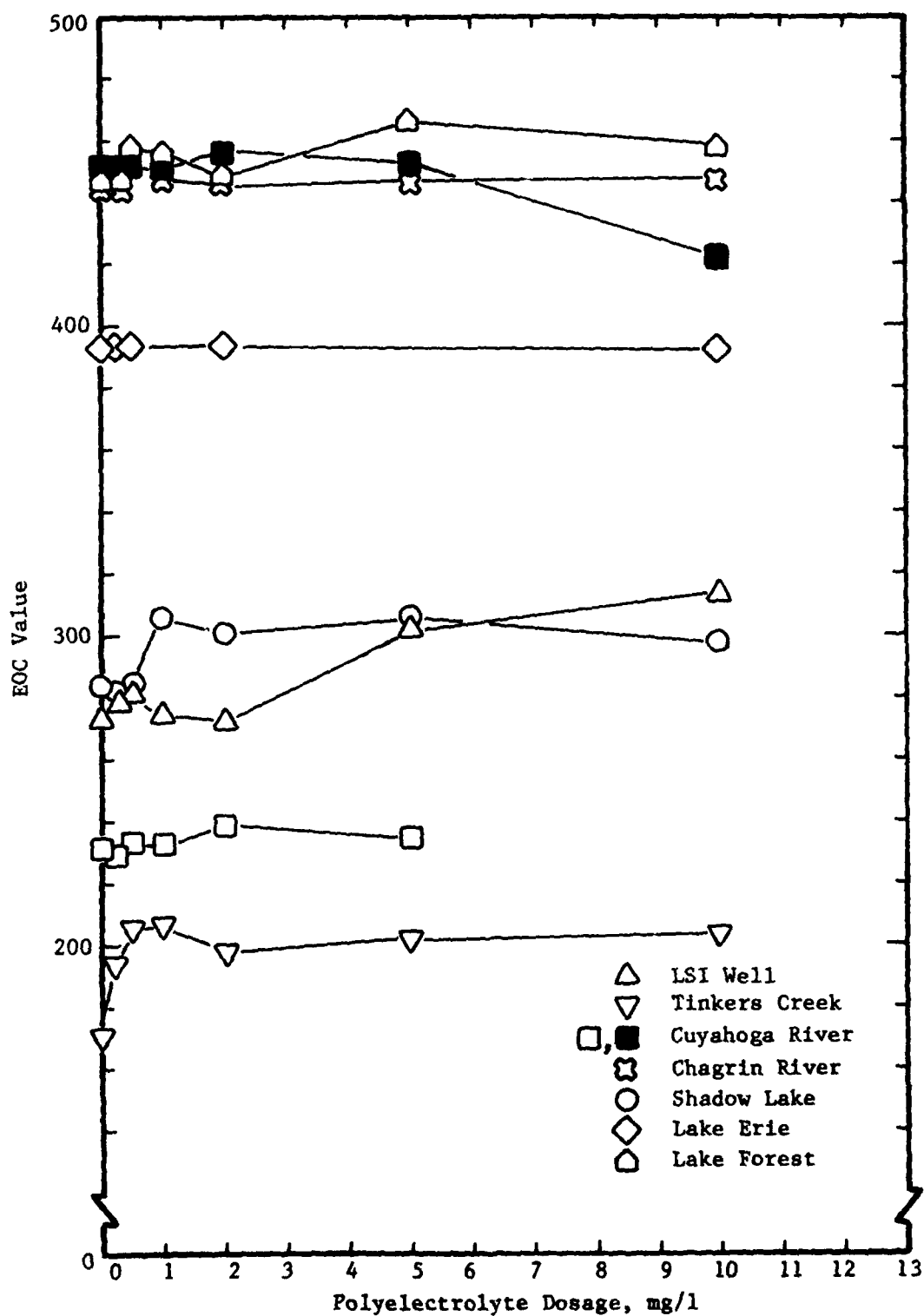
FIGURE 16   EOC VALUE VERSUS POLYELECTROLYTE DOSAGE
FOR NATURAL WATER FILTRATES
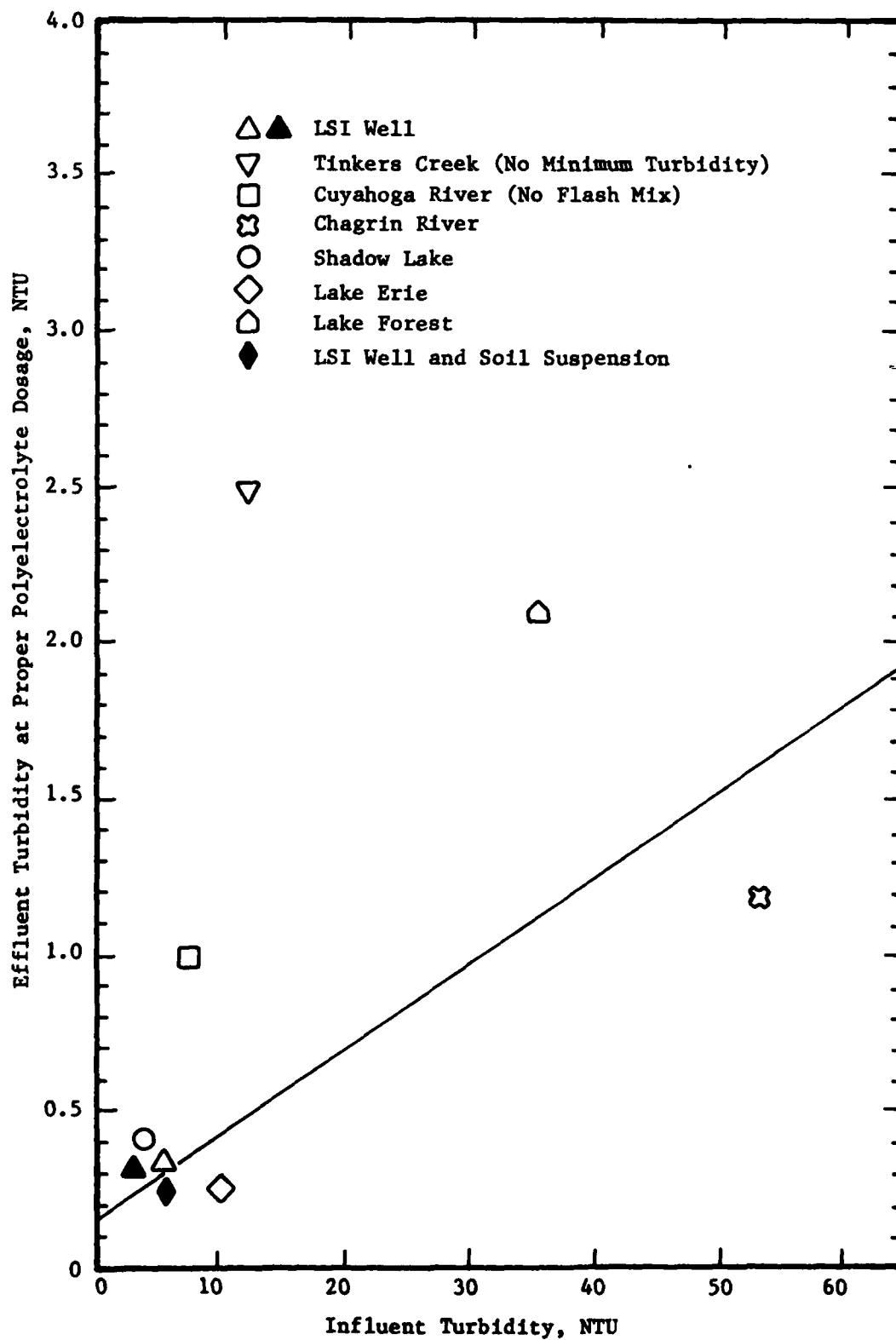
Life Systems, Inc.

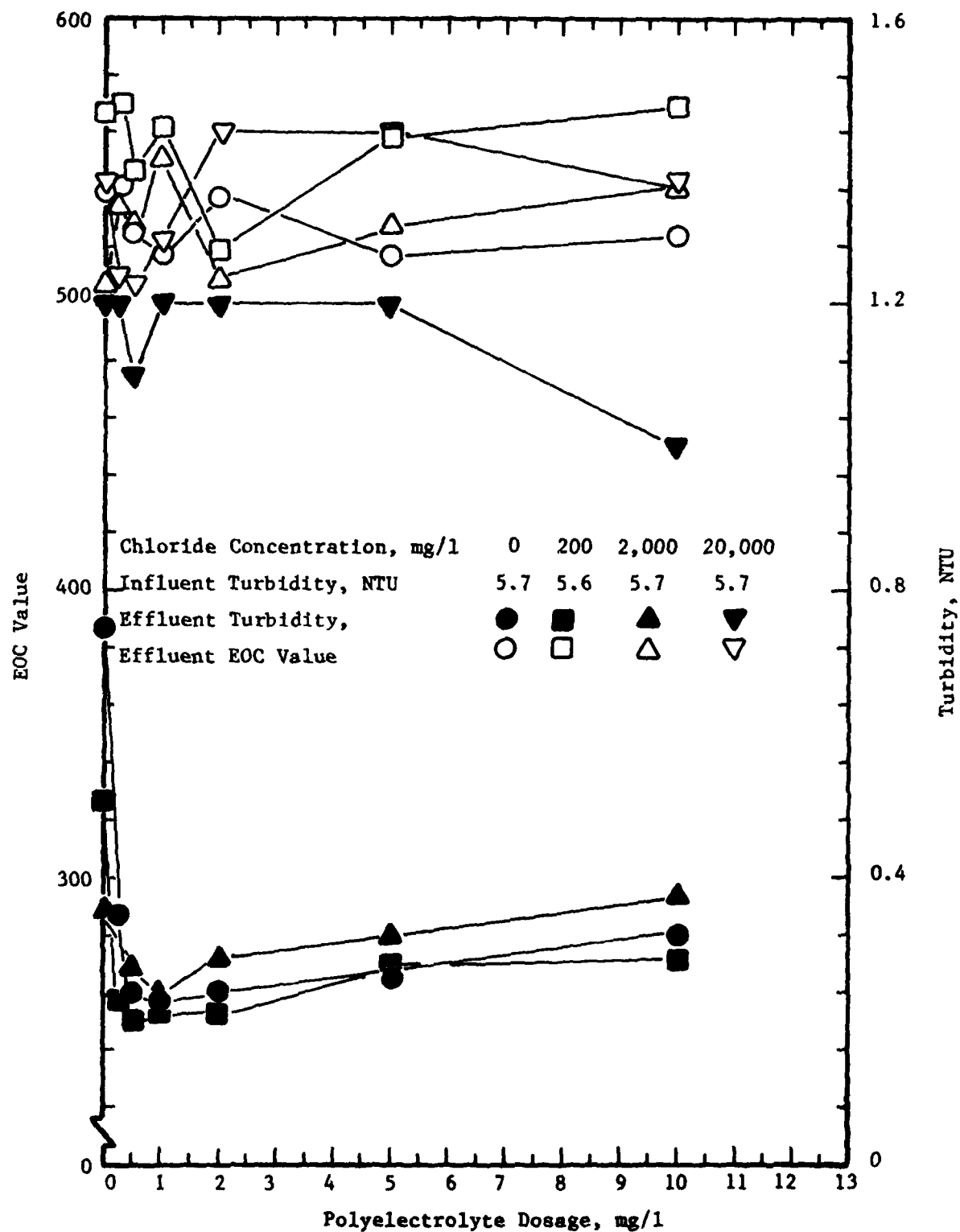FIGURE 17   ILLUSTRATION OF INFLUENT TURBIDITY EFFECT
ON EFFLUENT TURBIDITY

FIGURE 18   RESULTS OF CHLORIDE EFFECTS EXPERIMENT

which aids coalescence of very small suspended particles.[40] The filtration process is aided at higher Cl⁻ concentrations by adherence of the particulates to the media or to previously deposited particulates on the media.[42]. However, if the ionic content of the solution becomes too high, the particles become highly charged through adsorption of ions from the solution. This charge can become large enough that the ability of the polyelectrolyte to coalesce the particles is diminished. The turbidity of the filtrate therefore increases at very high Cl⁻ concentrations.

Instrument Stability Test

A drift test was performed to quantify the stability of the EOC Analyzer and on-line turbidimeter for monitoring the filter effluent. The optimum polyelectrolyte dosage for the single water sample used during the test was first determined. Filtration under those dosage conditions was then continued for 24 hours, during which the turbidities and EOC values were recorded with an on-line turbidimeter and the Breadboard EOC Analyzer. Filtrate turbidities were also checked with a standardized laboratory turbidimeter to enable drifts in the on-line turbidimeter to be distinguished from changes in effluent properties. The on-line turbidimeter was adjusted initially so that its reading corresponded to that of the laboratory turbidimeter. The results of this test are plotted in Figure 19.

The need for a method of calibrating the on-line turbidimeter is demonstrated by the fact that the turbidimeter output increased abruptly soon after the start of the test. Future turbidimeters used in the ROWPU should have, at a minimum, automatic zeroing capability, with automatic span calibration if possible.

The EOC Analyzer responded to the generally constant organic loading in the water, and the turbidity changes in the sample did not affect the EOC response. The EOC Analyzer also exhibited unusually large scatter in this test. It is possible that the electrode cleaning sequence produces a certain amount of bubbles on the indicating electrode. With this sample and polyelectrolyte, the amount of bubbles formed may be greater than for other samples. Because bubbles act in electrochemical cells as capacitors and EOC circuitry measures capacitance, the EOC data exhibits more fluctuations than it otherwise would. An adjustment to the electrode cleaning sequence is required to resolve this. However, this data in no way affects the overall conclusion that a turbidimeter, and not the EOC Analyzer, should be used in the ROWPU to monitor and control polyelectrolyte addition.

CONCLUSIONS

The survey of Army-related applications for the EOC Analyzer has been completed. An experimental evaluation of the Analyzer operating as a monitor of polyelectrolyte addition for coagulation and filtration of water in the ROWPU has demonstrated that the EOC Analyzer apparently responds with a high sensitivity to organics dissolved in natural water samples. Data obtained during this evaluation suggests that the EOC Analyzer could be used to monitor the concentration of these organics and the effectiveness of processes that remove those organics.
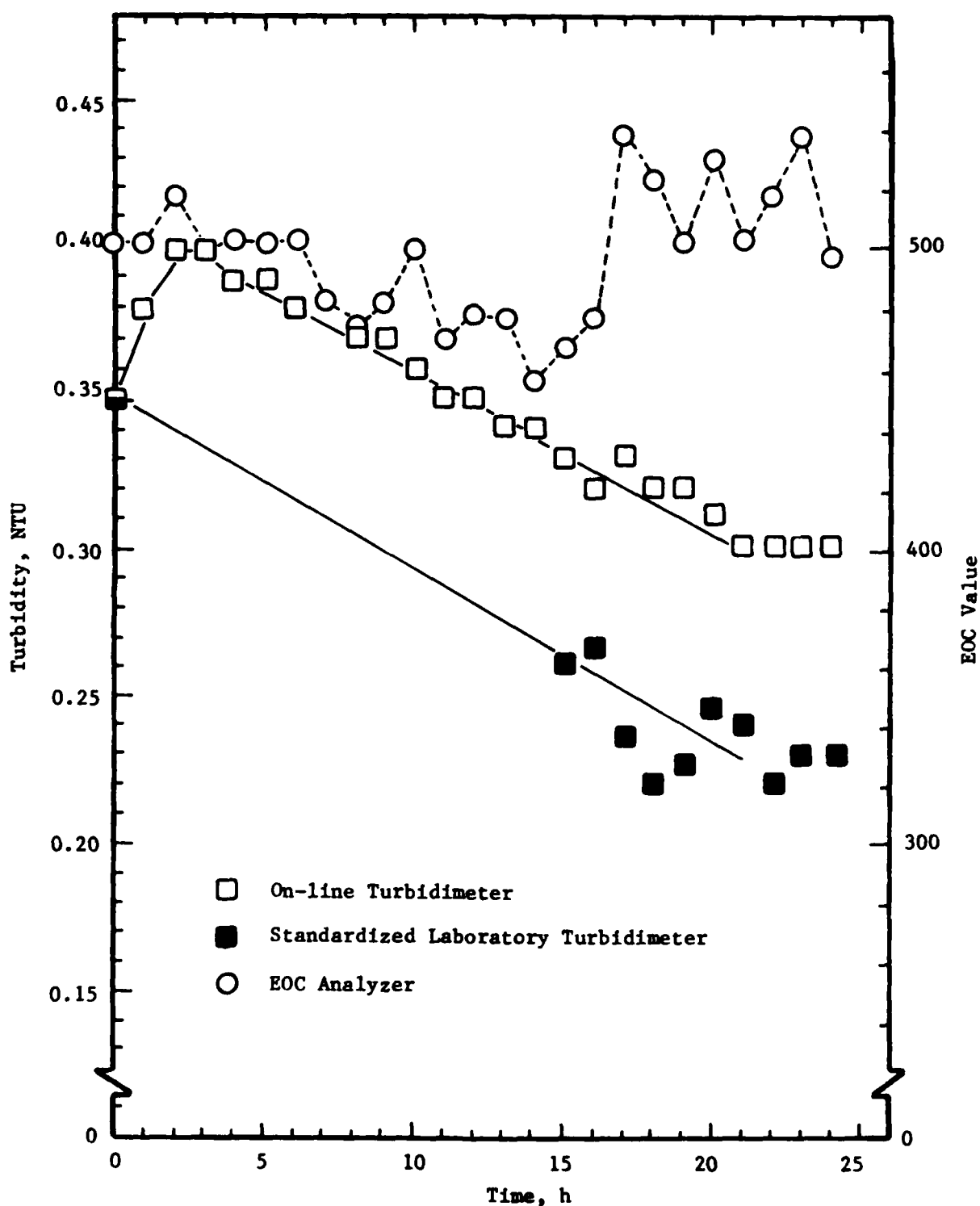
FIGURE 19   RESULTS OF ANALYZER DRIFT EXPERIMENT

The response of the Analyzer to these organics so overwhelmed its response to the polyelectrolyte, that the EOC Analyzer is unsuitable for the ROWPU application. Comparison tests performed with an on-line turbidimeter demonstrated that the turbidimeter could be used to control polyelectrolyte dosage if modifications were made to automatically calibrate the turbidimeter on a periodic basis. Other modifications are suggested to protect the optics of the turbidimeter from fouling or to provide means for simplified maintenance. Also, control logic is required to locate the minimum turbidity as a function of polyelectrolyte dosage, recognizing that the minimum turbidity will be different from one water sample to the next.

The survey of other EOC Analyzer applications identified four organic removal processes in which the EOC Analyzer could be used for control and monitoring purposes. These are:

1. Carbon and synthetic adsorbent column monitoring for detection of organic breakthrough and initiation of adsorbent regeneration.

2. Monitoring coagulation and sedimentation processes for removal of humic and fulvic acids from raw water prior to disinfection and use as drinking water.

3. Monitoring the influents and effluents of biological treatment processes for optimization of process performance.

4. Monitoring processes such as air flotation and oil skimming for oil and grease removal.

The development time and costs required for adapting the EOC Analyzer technology for each of these applications varies, depending upon the quality of the water that must be analyzed. The least investment would be required for the development of advanced versions of the EOC Analyzer to monitor adsorbent columns. Effluents from this type of source contain low concentrations of suspended solids, and fouling of the Analyzer due to buildup of particulates and microbiological growth would be minimal.

Similar conditions would exist in coagulation and sedimentation processes. However, polyelectrolytes or other coagulants would exist in the effluents of these processes, resulting in increased possibility of fouling.

Influents and effluents from biological processes would contain even more suspended solids and provide the capability of fouling through microbiological activity. Advanced Analyzers designed for this application would require filters or specialized features that make them compatible with samples from biological treatment systems.

The EOC Analyzer has never been tested as a monitor of oil and grease. While it can be expected to be responsive to these substances, the Analyzer would also encounter in this application the lowest quality samples of any of the four applications. The electrochemical cleaning sequence used to maintain the indicating electrode in the Analyzer in a reproducibly clean condition would be challenged more in this application than in any of the others.

On the basis of these considerations, it is concluded that the EOC Analyzer
will find its most appropriate Army-related uses in the monitoring of adsorbent
column effluents for the treatment of munitions wastes, metal finishing wastes,
physical-chemical wastewater treatment systems and water treatment systems
employing absorbent columns or coagulation and sedimentation processes for the
removal of trihalomethane precursors.

RECOMMENDATIONS

It is recommended that the EOC Analyzer be evaluated for use in monitoring the
effluents of absorbent columns and coagulation and sedimentation processes.
Use of the EOC Analyzer as a detector of organic breakthrough in adsorbent
columns, in order to minimize adsorbent regeneration costs while preventing
undetected organic discharge, seems especially suitable, and has a readily
definable economic advantage.

Before the Analyzer is adapted to this use, an extensive evaluation should be
performed of its analytical response to the organics in specific wastewaters.
A correlation between EOC response and the organic removal efficiency of the
process should be established. This would demonstrate the magnitude of the
response that would be obtained during organic breakthrough or other significant
changes in the process.

Tests performed with real effluents (and performed on-line, if possible) would
demonstrate the change in EOC response that would be obtained for normal
variations in parameters other than organic concentration (e.g., conductivity,
Cl$^-$ concentration and DO levels). These response changes must be small in
comparison to changes resulting from organic concentration variations to avoid
false indications of organic breakthrough and process failure.

The Breadboard EOC Analyzer delivered to MBRDL upon completion of Contract No.
DAMD17-75-C-5070 is compatible with use in this evaluation. A duplicate unit
also was assembled and is at Life Systems. Either of these Analyzers could be
used to effectively prove the usefulness of the EOC Analyzer for any specific
application. Then the design of the more advanced version of the Analyzer to
be used routinely would be based on application - specific factors such as
environmental conditions, manpower limitations and logistic requirements.

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